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Geochemistry, Mineralogy, and Stable Isotopic Results from Ala Wai Estuarine Sediments: Records of Hypereutrophication and Abiotic Whitings[1]

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ABSTRACT: The geochemistry, mineralogy, and stable isotopic composition of sediments cored from the Ala Wai Canal, described for the first time here, provide a record of past changes in salinity, oxygenation, and eutrophication in a shallow, subtropical artificial estuary. Sediments of the canal are rich in organic carbon (ca. 1–8%) and calcium carbonate (ca. 6–68%). The carbonate fraction contains a mixture of aragonite (ca. 2–25%), magnesian calcite (ca. 1–38%), and calcite (0–11%). The majority of this carbonate seems to be a direct result of biogenically induced inorganic precipitation from the water column. This interpretation is supported by historical measurements of hypereutrophication in the water column, the appreciable lack of biogenic carbonate in the sediments, the presence of carbonate throughout the canal, the fine grain size and mixed marine mineralogy of the carbonate, the significant positive correlation between $CaCO_3$ and uranium scavenged from the water column, the lack of detectable carbonate in associated fluvial sediments, the similarity between the isotopic composition of the carbonates and that of the total dissolved carbon in the present water column, and the positive covariance between accumulation rates of $CaCO_3$ and organic carbon in portions of the back basin core. Supersaturation with respect to these phases appears favored by high primary productivity and accompanying CO_2 drawdown in warm surface waters. The process of precipitation is analogous to marine whitings and inorganic $CaCO_3$ precipitation in lakes, but to our knowledge this is the first reported occurrence documented from an estuarine system. Temporal variations in paleoproductivity, bottom water oxygenation, and changes in the water balance of the canal are assessed on the basis of $CaCO_3$ and organic carbon flux rates and by downcore variations in the isotopic composition of organic carbon, $CaCO_3$, and benthic foraminifera. We demonstrate that the canal was, and continues to be, highly productive and that the back, landlocked basin of the canal has undergone episodes of progressive eutrophication at least twice since 1935. The first phase of eutrophication is marked by an upsection increase in the stable carbon isotopic gradient between surface and deep waters. During this time the back basin became hydrologically closed and its waters became fresher, as

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indicated by the compositions and covariance in carbon and oxygen isotopic values of the carbonates. The second phase began about the time that the canal's sediment sill was dredged and is marked by an upsection increase in the carbon isotopic composition of authigenic carbonates and benthic foraminifers, reflecting a progressive increase in primary productivity and water-column stratification through time. Oxygen isotope results suggest that the second phase is also marked by increased freshening of the back basin as the sediment sill has built back to the canal's surface.

THE ALA WAI CANAL is a partially mixed, moderately stratified artificial estuary created in 1927 to drain the low-lying wetlands in the tourist resort area of Waikīkī. Fifty meters wide near its mouth, the canal extends inland from the ocean for 0.75 km, makes a 45° bend, and ends 2.35 km after the bend, forming a landlocked back basin (Figure 1). The longer, landlocked section receives freshwater discharge from the Mānoa-Pālolo Stream drainage system. Originally dredged to a depth of 3–6 m, the mean depth of the canal in 1969 was estimated to be only 1.8 m (Gonzalez 1971). Today the canal contains four distinct features: a seaward-dipping channel extending for ca. 1 km inland from the mouth, a small basin having a maximum depth of 3.5 m between the Kalākaua Street and McCully Street bridges, a silled shoal region at the mouth of the Mānoa-Pālolo Stream, and a back basin, inland of the sill (Figures 1, 2). The sill at the mouth of the

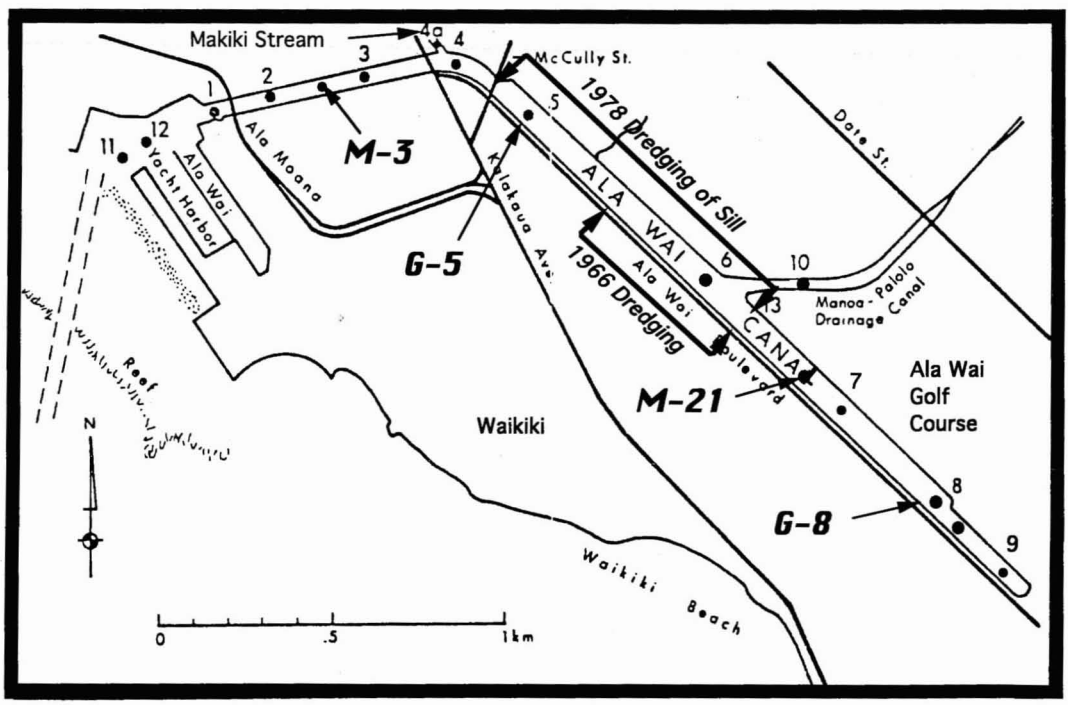

FIGURE 1. Location of sediment cores M-3, G-5, M-21, and G-8 taken from the Ala Wai Canal. Initial completion of the canal was in 1927. Since then, because of the persistent formation of a sedimentary sill at the mouth of the Mānoa-Pālolo Stream drainage canal, two segments of the canal were dredged in 1966 and 1978. The positions of these dredged segments are shown. Today, the canal contains another large sill at the mouth of the Mānoa-Pālolo Stream, and the bottom waters behind it (to the southeast) are dysaerobic. Normally oxygenated seawater enters the canal through the Ala Wai Yacht Harbor. Sites 1–13 of Gonzalez (1971) are also shown.

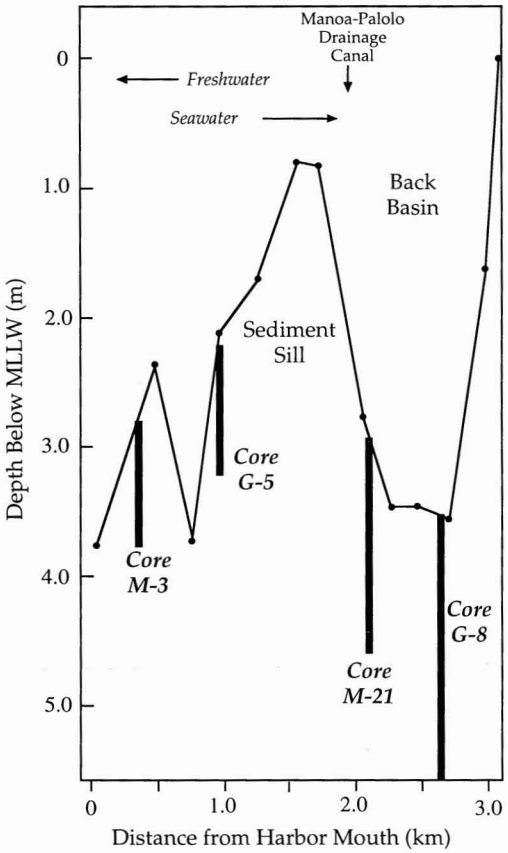

FIGURE 2. Bathymetry profile of the Ala Wai Canal in 1991 (after Laws et al. [1993]) and core locations.

Mānoa-Pālolo Stream becomes exposed at low tide although seawater still flows around it along its southwestern side. Since its creation, the canal has become a polluted, highly eutrophic body of water. To increase ventilation and combat pollution and siltation in the channel, the sill was removed by dredging in 1966 and 1978 (Gonzalez 1971, Department of Land and Natural Resources, State of Hawai'i 1990, Lum and Cox 1991, Laws et al. 1993). The 1966 dredging removed a length of ca. 0.5 km of the sill, and the 1978 dredging removed ca. 1.0 km (Figure 1). The back basin of the canal, which has been at least periodically dysaerobic to anoxic, was not dredged.

Large spatial and temporal variations characterize the salinity and temperature distributions in the canal. Annual average surface water salinity varies between 0 and 32 psu (primary salinity units, parts per thousand), depending on location, runoff, tidal stage, and wind conditions (Gonzalez 1971). A halocline is usually within 1 m of the surface, except during peak runoffs, when its bottom limit may extend to 2 m or more. Below the halocline, salinities are usually in the range of 33–34 psu throughout the canal (Laws et al. 1993). The temperature distribution in the canal is also strongly affected by the magnitude of the freshwater influx, and large vertical gradients of as much as 6°C m^{-1} have been observed during peak runoffs (Gonzalez 1971). The back basin, extending upstream from the sill, receives freshwater from neighboring streams that overrides seawater entering the canal from the Ala Wai Yacht Harbor (Figure 1). Salinity in the back basin remains high (surface water 28–32 psu; bottom water 32 psu [this study]), however, resulting in a dominantly marine environment. The water in this basin is also frequently warmer than elsewhere, sometimes by as much as 1°C, chiefly because of the absence of seaward transport of heat from the basin. This temperature difference also affects the renewal of water in the basin below sill depth. In 1969, when the sill was ca. 1 m deep, the average residence time of water behind the sill was calculated to be of the order of days to weeks (Gonzalez 1971). The waters behind the sill have been stratified with respect to salinity, temperature, and density (Gonzalez 1971). In addition, the oxygen levels in the back basin water have been lower than elsewhere in the canal, with dysaerobic to anoxic conditions occurring in the deepest waters of the basin ($O_2 < 1$ ml/liter throughout 1969 [Gonzalez 1971]). Furthermore, high concentrations of nutrients in the form of nitrate (2–8 μg-at/liter) and phosphate (0.1–3.4 μg-at/liter) occur in the canal with point sources at the Mānoa-Pālolo and Apukehau Streams and at a large storm drain at the extreme head of the canal (Gonzalez 1971, Harris 1975, Vink 1991 [pers. comm.], Laws et al. 1994). Nutrient loading from the adjacent Ala Wai Golf Course is another potential nonpoint-source input.

Recent studies by Laws et al. (1993) indicated that productivity indices in the Ala Wai Canal at 50-cm depth are close to the theoretical maximum of 25 g C g^{-1} chl *a* h^{-1} estimated by Falkowski (1981) and that conditions in the upper water column are close to optimal for phytoplankton growth. Diatom and dinoflagellate production increases toward the back basin and, with an average primary productivity rate of 5.3 g C m^{-2} d^{-1} (Harris 1975, Beach et al. 1995), the Ala Wai water column displays a hypereutrophia rivaled by few other natural water bodies in the world (e.g., Jellyfish Lake, Palau, 3.1 g C m^{-2} d^{-1} [Hamner et al. 1982]; Lake George, East Africa, 4–6 g C m^{-2} d^{-1} [Talling 1965]; Lake Maruit, Egypt, 3.4–7.7 g C m^{-2} d^{-1} [Aleem and Dowidar 1965]; major oceanic upwelling zones, <1.4 g C m^{-2} d^{-1} [Glenn and Arthur 1985]). Compared with these other occurrences, the small size, marine waters, simpler geometry, and the limited-input point sources for detritus combine to make the Ala Wai significant for modeling processes responsible for the delivery of organic carbon and nutrient elements to sediments. In this paper, we examine the sedimentary record of primary productivity and eutrophication in this canal. To this end, we measured the variations in the contents of organic carbon, calcium carbonate, sulfur, nitrogen, and uranium in the Ala Wai sediments as a function of time and examined these in relation to variations in nutrient contents and marine-versus-terrigenous organic sources. The sedimentary record of the stable isotopic composition of carbon in calcite, organic matter, and benthic foraminiferal tests and the oxygen isotopic composition of the carbonates and foraminifera have also been used to trace variations in productivity and eutrophication through time.

MATERIALS AND METHODS

This study concentrates on sediment cores obtained from four stations in the Ala Wai Canal, shown in Figures 1 and 2. The cores were obtained in the summer of 1991 by manually pushing 6-m-long core-liner sections into the sediments from a small boat positioned near the center of the canal at each station. Total lengths of 90 cm of core were obtained at station M-3, 85 cm at station G-5, 162 cm at station M-21, and 200 cm in the back basin at station G-8. The water depths at those stations at the time of coring were 3.8, 3.0, 3.0, and 3.1 m, respectively (Figure 2). After coring, the cores were sealed with rubber stoppers and immediately transported vertically a few miles to the University of Hawai'i cold storage (2°C) core repository. The cores were then frozen and split with a table saw. Visual core description was carried out immediately after splitting the cores, although some of the primary fabric of the cores may have been lost as a result of ice crystallization during the freezing process. Most of our studies have concentrated on core G-8 because of its recovery length and because of its location beneath waters displaying highest primary productivity, stratification, and oxygen deficiency.

Selected samples were examined as smear slides with the petrographic microscope and as carbon- and gold-coated samples using a scanning electron microscope (SEM) (Zeiss DSM 962). X-ray diffraction (XRD) mineralogy analyses of the Ala Wai sediments were performed with an X-ray diffractometer (Scintag PADV) using Cu-Kα radiation. Size-separated, glycolated and unglycolated bulk powder and oriented glass-slide mounts were compared for determination of clay mineralogy on selected samples that were subjected to carbonate removal by sodium acetate–acetic acid buffer solution (Jackson 1974). Quantitative proportions of carbonate mineral phases were determined by comparing XRD peak areas using the methods of Sabine (1992). Magnesium contents were determined by the methods of Neumann (1965).

Representative sediment samples were analyzed for inorganic and organic carbon, total sulfur, total nitrogen, and uranium-238. Total carbon, carbonate carbon, and total sulfur were determined by coulometric titrations (cf. Huffman 1977, Engleman et al. 1985). Percentage total organic carbon (TOC) was calculated by difference between total (combustible) carbon (organic carbon plus

carbonate carbon) and carbonate (acid-soluble) carbon (C_{CO_3}). Assuming that total inorganic carbon (TIC) has the stoichiometry of pure $CaCO_3$, calcium carbonate contents were calculated from the TIC data. Nitrogen was determined with a CHN analyzer (Perkin-Elmer Model 2400) (Sharps 1974). Uranium-238 concentrations were calculated on the basis of gamma counting measurements of thorium-234 (discussed in detail in McMurtry et al. [1995]).

Isotopic analyses of carbon and oxygen were carried out on selected samples from core G-8, following the traditional phosphoric acid method (McCrea 1950). Dried, bulk sediments were reacted in anhydrous H_3PO_4 ($\rho = 1.92$ g cm^{-3}) at 50°C for 1 hr, and the evolved CO_2 was cryogenically purified before analyses on Finnigan Mat 25 and Finnigan delta S stable isotope mass spectrometers. Oxygen isotopic enrichments were corrected for ^{17}O contamination (Craig 1957) and converted relative to the PDB carbonate standard. The reproducibility of the isotopic composition based on replicate measurements is of the order of $\pm 0.10‰$ for $\delta^{13}C$ and $\pm 0.15‰$ for $\delta^{18}O$. The isotopic composition of bulk organic carbon was determined by mass spectrometric analysis of CO_2 produced by combustion of acid-treated (50% HCl) samples at 850°C for >8 hr using CuO as an oxidant. Subsamples from the same levels in the core were used for both carbonate and organic carbon analyses. In addition, isotopic analyses of benthic foraminiferal tests of the genus *Quinqueloculina* (cf. Resig et al. 1995) from several horizons in core G-8 were also performed. All isotopic results are expressed in conventional values with respect to the PDB standard.

Mass sedimentation rates were found by radiometrically dating 4-cm sections covering the upper 116 cm of the core G-8 from the back basin area, using cesium-137. Details of the cesium-137 technique and systematics are presented in McMurtry et al. (1995). Ages were calculated for the midpoints of each of the sections dated. A mean sedimentation rate of 3.43 cm yr^{-1} was found for core G-8, which agrees rather well with Gonzalez's (1971) estimate of 7×10^3 m^3 yr^{-1} (= 3.5 cm yr^{-1}) based on changes in bathymetry during the 40 months following the canal dredging in 1966, and the sedimentation rate of 8×10^3 m^3 yr^{-1} estimated by Laws et al. (1993). However, mean sedimentation rates in the central part of the core (between 65 and 155 cm) are unusually high, with rates >20 cm yr^{-1} at 100-cm depth. Below 116 cm, where age data were not available, we have assumed a sedimentation rate of 3.43 cm yr^{-1}. This would assign an age date of ca. 1933 for the bottom of the 2-m core G-8. Because fine-scale interpretations of the cesium-137 data may change with our ongoing modeling studies (McMurtry et al. 1995), we first report our results with respect to variations with depth in the sediments and subsequently recast these in terms of our interpretations of variations with time.

Accumulation rates of $CaCO_3$ and organic carbon (C_{org}) in mole cm^{-2} yr^{-1} were calculated as follows:

$$E_{acc.rate} = \frac{(cE)\rho S}{100E_{AW}}$$

where $E_{acc.rate}$ = accumulation rate of the element or compound, c = weight percentage of the element or the compound, E_{AW} = atomic weight of the element or molecular weight of the molecule, ρ = the dry bulk density of the sediment in g cm^{-3}, and S = bulk sedimentation rate in cm yr^{-1} (cf. Glenn and Arthur 1985).

RESULTS

Mineralogy

Sediments of the Ala Wai Canal are relatively dark brown to black muds displaying little internal bedding (Figure 3). They are not laminated and become silty near the Ala Wai Yacht Harbor. They become light gray with increasing proportions of calcium carbonate. XRD analyses and optical examination of the sediments show them to be predominantly a mixture of microcrystalline carbonate muds and detrital clays (smectite and chlorite) with abundant diatom tests and pyrite, and various admixtures of detrital

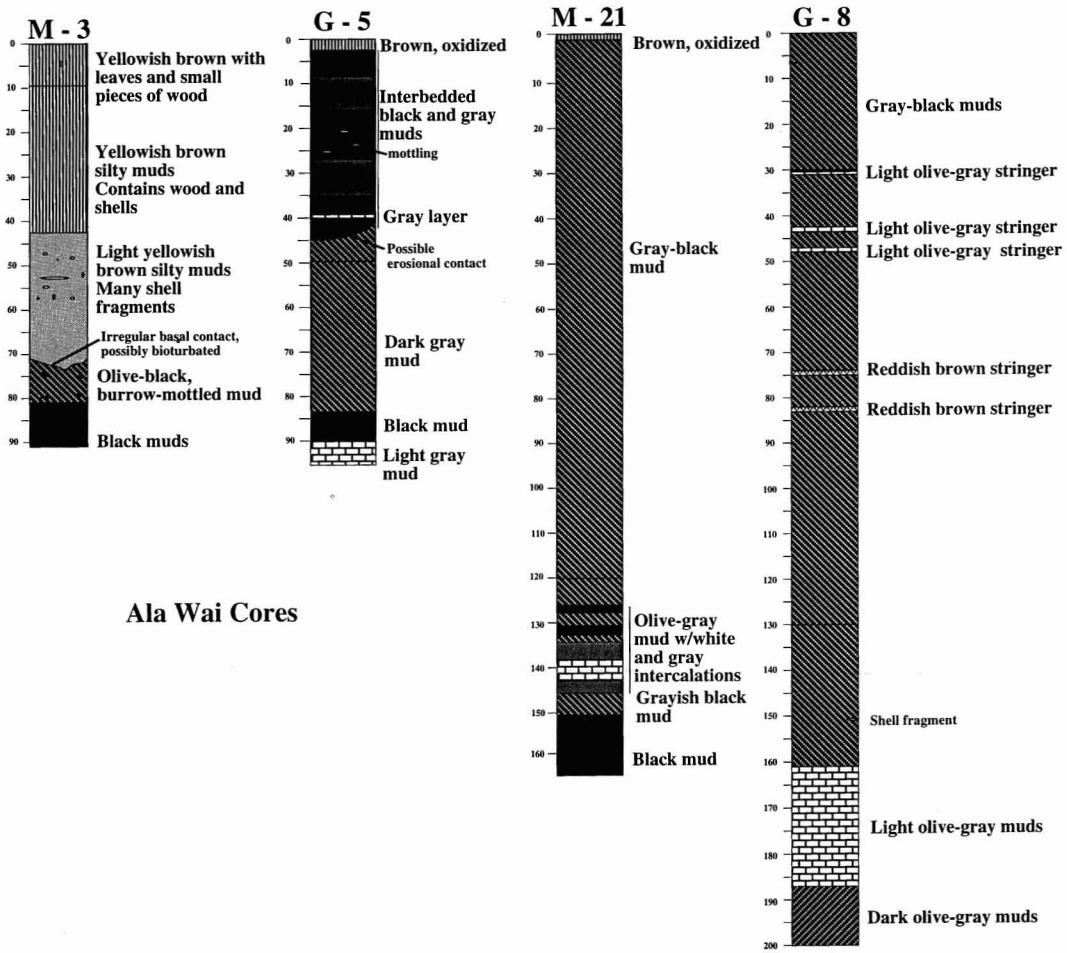

FIGURE 3. Lithologic logs of sediment cores M-3, G-5, M-21, and G-8 taken from the Ala Wai Canal (depth in centimetres).

feldspars, rock fragments, benthic foraminifers, sponge spicules, and fish scales and bones throughout all the cores. Nearly all the foraminifera and diatom tests contained some degree of pyrite filling; many were completely infilled (cf. Resig et al. 1995). Some unconfined euhedral pyrite grains were also observed. Magnetite was found in small quantities in some of the XRD analyses. The carbonate component of the muds is a covarying mixture of aragonite (ca. 2–25%), magnesium-rich (magnesian) calcite (ca. 1–38%) with ca. 14 mole % $MgCO_3$, and calcite (ca. 0–11%) with ca. 1–3 mole % $MgCO_3$. The origin of these phases is discussed below.

Contents and Accumulation Rates of Carbonate and Organic Matter

Geochemical results from the Ala Wai cores are given in Tables 1 and 2. Figures 4 and 5, respectively, illustrate the variations in calcium carbonate ($CaCO_3$) and organic carbon (C_{org}) contents in the Ala Wai cores. Except where directly diluted by terrigenous components, bulk calcium carbonate concentrations form a nontrivial proportion of the

Ala Wai sediments. Both in the surface sediments and downcore, carbonate contents are lowest in core G-5 at the front of the midcanal sill where the sediments are most strongly diluted by inputs of siliciclastic detritus. Elsewhere, the cores display calcium carbonate contents generally in excess of 5–10 weight percentage (%). Highest carbonate values occur in the back basin (core G-8) where background values are ca. 10%. In addition, two intervals very rich in carbonate (totaling 20–80% $CaCO_3$) occur in core G-8 between 25 and 50 cm and between 160 and 200 cm (Figure 4). The carbonate between 160 and 200 cm of core G-8 occurs as a massive layer whereas the elevated carbonate contents between 25 and 50 cm occur as thin (ca. 0.5 cm) gray interbeds occurring at 30, 43, and 47.5 cm (Figures 2 and 3). Sediment samples from the Mānoa-Pālolo Stream were also analyzed and, although crossing exposed fossil reef materials, were found to contain no calcium carbonate minerals. This is likely a result of the chemical rather than physical weathering of these stream-bed outcrops.

Distinctly high organic carbon contents, with values ranging between 1 and 4%, are characteristic of all the cores retrieved from the canal (Figure 5). Maximum values of 4–6% are concentrated in the top 50 cm of the sediment sequence in all four cores. A gradual downcore decrease in organic carbon content is conspicuous in all the cores examined. Because of dilution effects, the three carbonate-rich gray layers in core G-8 show an abrupt decrease in organic carbon by ca. 2% relative to the mean value.

Figure 6 illustrates that the carbonates of the Ala Wai sediments are actually an intimate mixture of extremely fine-grained low magnesium calcite (1.2–3.3 mole % $MgCO_3$), magnesian (high magnesium) calcite (12.8–16.2 mole % $MgCO_3$), and aragonite. These three phases occur as submicron-sized particles not individually resolvable with the SEM (<0.1 μm). Very little of the total carbonate occurs as foraminiferal calcite. Based on the number of foraminifers per gram of sediment (Resig et al. 1995) and the average weight of these foraminifers (ca. 50 μg per individual), we calculate that the foraminifers of core G-8 contribute $<1\%$ of the total sediment $CaCO_3$. In addition, the number of foraminifers per gram of sediment actually decreases with increasing proportions of total carbonate.

Molar accumulation rates of $CaCO_3$ and organic carbon (C_{org}) for core G-8 indicate that the rates vary between 0.02–1.45 moles cm^{-2} yr^{-1} and 0.02–3.66 moles cm^{-2} yr^{-1}, respectively, with maximum values for $CaCO_3$ in the core sections between 25–50 cm, 80–115 cm, and below 150 cm (Figure 7). The accumulation rates of C_{org}, on the other hand, are anomalously high only between ca. 85 cm and 115 cm, near the middle of the core. A strong positive correlation, discussed below, occurs between $CaCO_3$ and C_{org} accumulation rates in the top 25 cm of these sediments and between 50 and 150 cm. Below 150 cm, the two rates show a weak negative correlation. However, because of our limited age constraints below 150 cm, the numerical values of accumulation rates below this depth should be viewed with caution.

Uranium Contents and Correlation with Calcium Carbonates

Uranium-238 occurs in the Ala Wai sediments in concentrations that range from ca. 1 to 26 ppm. These concentrations are unusually high for carbonate or siliceous sediments. Surprisingly, U in Ala Wai sediments proportionally covaries with % $CaCO_3$ (Figure 8) and, like $CaCO_3$, is diluted by increases in C_{org}. We say this is surprising because most carbonates typically contain little U. Limestones, dolomites, and other sedimentary carbonates are generally considered to be among the least uraniferous of all rocks of the earth's crust, containing from almost none to up to ca. 4 ppm (Bell 1963). Foraminiferal calcite, for example, usually contains <1 ppm; live scleractinian corals, composed of aragonite, may contain 2.5–3.0 ppm; and other marine carbonate-secreting organisms contain less than this amount (e.g., Ku 1965, Cross and Cross 1983, Delaney and Boyle 1983, Chung and Swart 1990). Similarly, non-

TABLE 1

GEOCHEMISTRY OF CORE G-8

DEPTH (cm) RANGE TOP	YEAR	SEDIMENTATION RATE (cm yr^{-1})	DRY BULK DENSITY (g cm^{-3})	WEIGHT % $CaCO_3$	WEIGHT % C_{org}	WEIGHT % N	WEIGHT % S	C/S	$CaCO_3$ ACC. RATE (M cm^{-2} yr^{-1})	C_{org} ACC. RATE (M cm^{-2} yr^{-1})	U ACC. RATE (μM cm^{-2} yr^{-1})	$\delta^{13}C$ CALCITE (‰)	$\delta^{18}O$ CALCITE (‰)	$\delta^{13}C_{org}$ (‰)	$\delta^{13}C$ FORAM. (‰)	$\delta^{18}O$ FORAM. (‰)
0.0	1992	0.00	0.117	8.91	5.50	0.54	2.06	2.67	0.00	0.00	0.00				−2.87	−2.47
4.0	1991	8.00	0.209	10.66	4.71		2.54	1.85	0.18	0.66	1.24	−0.99	−3.55	−23.54		
5.0	1990	0.91	0.209	11.16	4.48	0.81			0.02	0.07						
8.0	1989	2.50	0.198	9.50	4.44	0.45	2.79	1.59	0.05	0.18	0.71				−3.27	−2.94
12.0	1988	5.71	0.215	10.08	4.50	0.44	2.95	1.53	0.12	0.46	1.81					
15.0	1988	6.00	0.215	13.08	3.88		3.23	1.20	0.17	0.42		−1.68	−2.87	−24.10	−4.34	−4.37
16.0	1987	0.91	0.245	12.41	3.93	0.41	3.16	1.24	0.03	0.07	0.18					
20.0	1985	3.08	0.201	13.33	3.64	0.4	3.24	1.12	0.08	0.19	0.60				−5.49	−5.46
24.0	1983	1.67	0.222	19.58	3.20	0.4	3.11	1.03	0.07	0.10	0.63					
28.0	1982	5.71	0.213	32.07	2.47	0.35	2.84	0.87	0.39	0.25	2.45					
30.0	1982	4.00	0.213	59.31	1.11	0.29	1.91	0.58	0.50	0.08				−22.73		
32.0	1981	1.82	0.179	15.33	3.48	0.39	3.72	0.94	0.05	0.09	0.90	−2.04	−2.71	−23.24		
36.0	1980	10.00	0.177	19.49	3.19	0.39	3.28	0.97	0.34	0.47	6.63				−5.04	−5.72
40.0	1979	3.64	0.180	10.50	3.46	0.37	3.75	0.92	0.07	0.19	1.77					
43.0	1979	6.00	0.180	80.38	0.60	0.65	0.86	0.70	0.87	0.05						
44.0	1978	1.43	0.222	33.15	2.15	0.3	2.77	0.78	0.11	0.06	1.19					
47.5	1977	7.00	0.222	67.81	1.94	0.32	1.24	1.56	1.05	0.25		−2.43	−2.31			
48.0	1976	0.56	0.223	24.91	2.13	0.27	2.71	0.79	0.03	0.02	0.67					
52.0	1973	1.29	0.240	10.08	2.94	0.36	2.72	1.08	0.03	0.08	0.53				−7.93	−7.47
54.0	1973	4.00	0.240	6.25	1.05		3.40	0.31	0.06	0.08						
56.0	1969	0.57	0.199	6.25	2.95	0.36	3.01	0.98	0.01	0.03	0.20				−4.07	−1.96
60.0	1966	1.25	0.227	8.41	2.55	0.35	2.71	0.94	0.02	0.06	0.35				−7.50	−6.06
64.0	1964	2.22	0.238	7.58	2.69	0.34	2.40	1.12	0.04	0.12	0.52					
65.0	1964	8.00	0.238	6.75	2.53		2.28	1.11	0.13	0.40					−4.75	−1.69
68.0	1964	8.00	0.248	7.16	2.51	0.36	2.58	0.97	0.14	0.41	2.81				−5.30	−1.19
72.0	1963	10.00	0.205	8.00	2.32	0.33	2.93	0.79	0.16	0.40	2.95					
76.0	1963	7.66	0.266	8.08	2.16	0.27	2.28	0.95	0.16	0.37	1.70					
78.0	1963	7.66	0.266	7.91	2.46		2.88	0.85	0.16	0.42						
80.0	1962	6.32	0.240	7.00	2.21	0.32	2.37	0.93	0.11	0.28	2.13				−5.77	−1.53
84.0	1960	1.60	0.290	8.00	2.09	0.3	1.69	1.24	0.04	0.08	0.59					
88.0	1959	16.00	0.289	9.91	2.15	0.32	1.73	1.24	0.46	0.83	6.14					
92.0	1959	16.00	0.256	10.16	2.17	0.33	2.10	1.03	0.42	0.74	5.42				−6.06	−4.44
96.0	1959	16.00	0.284	7.16	2.64	0.32	1.94	1.36	0.33	1.00	4.51					
98.0	1959	72.00	0.284	7.00	2.15		1.71	1.26	1.43	3.66		−3.19	−3.04	−22.67		
100.0	1959	4.80	0.288	8.87	2.14	0.31	2.03	1.05	0.12	0.25	1.24				−5.66	−2.24
104.0	1959	40.00	0.290	10.16	2.12	0.32	2.35	0.90	1.18	2.05	12.96					
108.0	1959	40.00	0.270	13.08	2.30	0.38	2.78	0.83	1.41	2.07	15.75			−22.96		
112.0	1958	20.00	0.260	14.91	2.30	0.37	2.78	0.83	0.77	1.00	8.06					
116.0	1958	6.87	0.277	15.70	2.24	0.36	2.93	0.76	0.30	0.35	3.28					
118.0	1957	3.43	0.277	16.78	1.57		2.82	0.56	0.16	0.12						
120.0	1957	3.43	0.284	13.49	2.19	0.36	2.55	0.86	0.13	0.18	1.44				−0.25	−1.31
124.0	1956	3.43	0.242	23.16	2.46		3.37	0.73	0.19	0.17	2.99				0.40	−3.02
128.0	1954	3.43	0.255	16.29	3.08	0.36	3.33	0.92	0.14	0.22	2.60	0.07	−3.01	−22.70		
132.0	1953	3.43	0.318	14.41	1.80	0.31	1.98	0.91	0.16	0.16	2.23					
136.0	1952	3.43	0.338	13.29	2.04	0.33	1.72	1.19	0.15	0.20	2.36					
138.0	1951	3.43	0.338	14.24	2.07		1.60	1.29	0.16	0.20		0.90	−2.51	−23.17		
140.0	1951	3.43	0.397	7.66	2.03	0.28	1.45	1.40	0.10	0.23	2.36	0.32	−2.90	−23.48	1.29	−2.04

TABLE 1 (continued)

DEPTH (cm) RANGE TOP	YEAR	SEDIMENTATION RATE (cm yr^{-1})	DRY BULK DENSITY (g cm^{-3})	WEIGHT % $CaCO_3$	WEIGHT % C_{org}	WEIGHT % N	WEIGHT % S	C/S	$CaCO_3$ ACC. RATE (M cm^{-2} yr^{-1})	C_{org} ACC. RATE (M cm^{-2} yr^{-1})	U ACC. RATE (μM cm^{-2} yr^{-1})	$\delta^{13}C$ CALCITE (‰)	$\delta^{18}O$ CALCITE (‰)	δ^{13} C_{org} (‰)	$\delta^{13}C$ FORAM. (‰)	$\delta^{18}O$ FORAM. (‰)
144.0	1950	3.43	0.329	9.50	2.43	0.26	1.39	1.75	0.11	0.23	1.71					
148.0	1949	3.43	0.327	16.20	1.88	0.29	2.05	0.92	0.18	0.18	2.21	0.95	−2.51		1.77	−2.06
152.0	1947	3.43	0.326	6.25	1.90	0.28	1.75	1.09	0.07	0.18	1.62			−23.64		
153.0	1947	3.43	0.326	5.41	1.65		1.84	0.90	0.06	0.15		0.95	−2.44		−0.57	−2.03
156.0	1946	3.43	0.321	6.41	2.15	0.31	1.74	1.24	0.07	0.20	1.17					
160.0	1945	3.43	0.327	44.65	1.51	0.25	2.52	0.60	0.50	0.14	5.55				−1.60	−4.72
164.0	1944	3.43	0.491	61.06	1.01	0.19	0.72	1.40	1.03	0.14	12.18					
167.0	1943	3.43	0.491	59.98	0.91		1.26	0.72	1.01	0.13				−22.57		
168.0	1943	3.43	0.517	59.48	1.03	0.22	1.22	0.84	1.05	0.15	10.34	1.55	−2.20			
172.0	1942	3.43	0.385	60.56	0.91	0.2	1.13	0.81	0.80	0.10	8.43					
176.0	1940	3.43	0.494	61.35	0.91	0.21	0.87	1.05	1.04	0.13	10.27					
177.0	1940	3.43	0.494	60.39	0.99		0.91	1.09	1.02	0.14						
180.0	1939	3.43	0.417	61.06	1.16	0.21	0.98	1.18	0.87	0.14	9.47					
184.0	1938	3.43	0.607	68.47	0.70	0.21	1.05	0.67	1.42	0.12	22.67				−1.05	−2.03
187.0	1937	3.43	0.607	56.73	1.00		1.01	0.99	1.18	0.17						
188.0	1937	3.43	0.397	55.81	1.51	0.21	0.79	1.91	0.76	0.17	10.44					
192.0	1936	3.43	0.414	51.65	1.20	0.23	1.08	1.11	0.73	0.14	10.59					
195.0	1935	3.43	0.414	52.56	1.13		0.96	1.18	0.75	0.13						
196.0	1935	3.43	0.565	52.23	1.12	0.21	0.98	1.14	1.01	0.18	12.89					

TABLE 2

GEOCHEMISTRY OF CORES M-3, M-21, AND G-5

DEPTH (cm) RANGE TOP	WEIGHT % $CaCO_3$	WEIGHT % C_{org}	WEIGHT % S
Core M-3			
0	6.74	5.36	1.05
4	7.74	6.53	1.18
8	12.99	6.38	1.32
12	11.74	6.19	1.57
16	5.41	6.57	1.82
20	13.41	4.84	1.90
24	7.91	3.52	1.86
28	9.16	2.65	1.40
32	6.08	2.90	1.23
36	7.66	2.08	1.23
40	11.74	2.85	1.40
44	11.16	3.11	1.91
48	8.74	3.26	1.87
52	11.74	3.40	1.47
56	12.32	3.11	1.37
60	14.82	3.09	1.41
64	10.24	2.95	1.24
68	16.65	3.27	1.66
72	31.81	1.93	0.94
76	24.06	2.35	1.00
80	15.15	2.37	1.31
84	4.41	2.97	2.10
87	8.58	3.84	2.52
Core M-21			
0	7.99	5.27	1.49
4	11.07	4.93	1.50
8	7.41	5.59	2.00
12	3.16	5.77	1.95
16	4.75	6.10	2.70
20	4.50	5.91	2.52
24	5.66	5.78	2.47
28	6.08	5.93	2.59
32	6.49	5.95	2.66
36	9.83	5.55	2.66
40	9.58	5.17	3.25
44	9.83	5.67	2.73
48	5.91	5.41	2.95
52	6.66	5.11	3.77
56	8.91	4.91	3.07
60	7.41	4.89	3.24
64	6.83	4.91	3.24
68	6.91	4.33	2.90
72	7.74	4.06	2.38
76	4.00	4.63	2.47
80	5.25	3.96	2.58
84	7.66	3.01	2.05
88	6.74	2.76	2.38
92	7.49	2.70	1.82
96	8.58	2.61	2.08
100	8.24	2.34	2.51
104	9.58	2.24	2.08
108	3.33	2.17	3.37

TABLE 2 (continued)

DEPTH (cm) RANGE TOP	WEIGHT % $CaCO_3$	WEIGHT % C_{org}	WEIGHT % S
112	4.00	2.19	1.50
116	2.25	2.68	1.21
120	5.83	2.69	1.15
124	14.74	2.41	1.17
128	8.24	2.60	1.20
132	23.06	2.02	2.05
136	40.30	1.79	1.20
140	14.65	2.38	1.24
144	6.16	2.79	1.15
148	6.16	2.63	0.91
152	5.33	2.54	1.87
156	6.00	2.10	1.26
160	4.91	2.18	1.23
Core G-5			
4	1.42	5.79	
14	5.75	5.12	
24	9.16	5.49	
34	1.92	7.73	
45	1.92	6.39	
54	7.83	5.03	
64	6.00	3.78	
74	6.50	2.56	
84	10.41	2.40	

skeletal aragonitic carbonates (ooids, peloids, carbonate muds) generally contain 1.5–3.5 ppm U. We are currently unsure which carbonate phase(s) (aragonite, magnesian calcite, calcite) in the Ala Wai house this U. Figure 8 suggests that U may co-occur with all these phases, but this suggestion is inconclusive because all three carbonate phases covary with one another (Figure 6). The adsorption of U by $CaCO_3$ is discussed further below.

Organic Carbon/Nitrogen

Different groups of organisms produce organic matter with different C and N contents. Organic nitrogen occurs preferentially in proteins and nucleic acids that are relatively abundant in phytoplankton and bacteria. Autochthonous marine organic matter is therefore characterized by relatively low C/N ratios, typically between 6 and 10. Similarly, the mean C_{org}/N for marine plankton is around 6 (Stein 1991). Lignin and cellulose, the dominant components of terrestrial vegetation, are relatively nitrogen-poor, so that allochthonous organic matter tends to have higher C/N ratios (Talbot and Johannessen 1992). Thus, these ratios provide some information about the composition of the organic matter preserved in the sediments, and the degree of mixing of terrigenous and aquatic organic carbon.

At site G-8, most of the atomic C/N ratios vary between 5 and 10, suggesting a mixed marine/terrigenous type of organic matter with a dominance of the terrigenous fraction (Figures 7 and 9; cf. Stein 1991, Talbot and Johannessen 1992). Closer inspection of the values suggests a distinct upcore progression in the terrigenous influx (Figure 7). The sediment sequence below 156 cm has a dominantly marine signature, with most of the C/N ratios clustering around 6. A fairly good correlation between higher concentrations of organic carbon and higher C/N ratios suggests that terrigenous influx of organic matter has indeed added to the endogenous organic fraction (Figure 9*B*). Studies by Laws et al. (1993) also indicated that the present-day flux of allochthonous organic carbon exceeds photosynthetic rates by ca. 60%. As discussed below, this factor has to be borne in mind while interpreting organic carbon signals in the sediment record in terms of marine primary productivity. The low C/N ratios of <6 are unusual, and it is noteworthy that these values characterize sediments with low organic carbon contents (C_{org} $<1\%$; Figure 9). C/N ratios for such organic-lean sediments may not always be reliable because it is possible that in these sediments the bulk of total nitrogen is in the form of inorganic or organic nitrogen-bearing compounds (ammonium ions, acetic acid, or amines) sorbed by clays (cf. Müller 1977, Stein 1991).

Organic Carbon/Total Sulfur Ratios

The sediment sequence in the back basin of the canal is generally enriched in sulfur relative to sediments with comparable organic

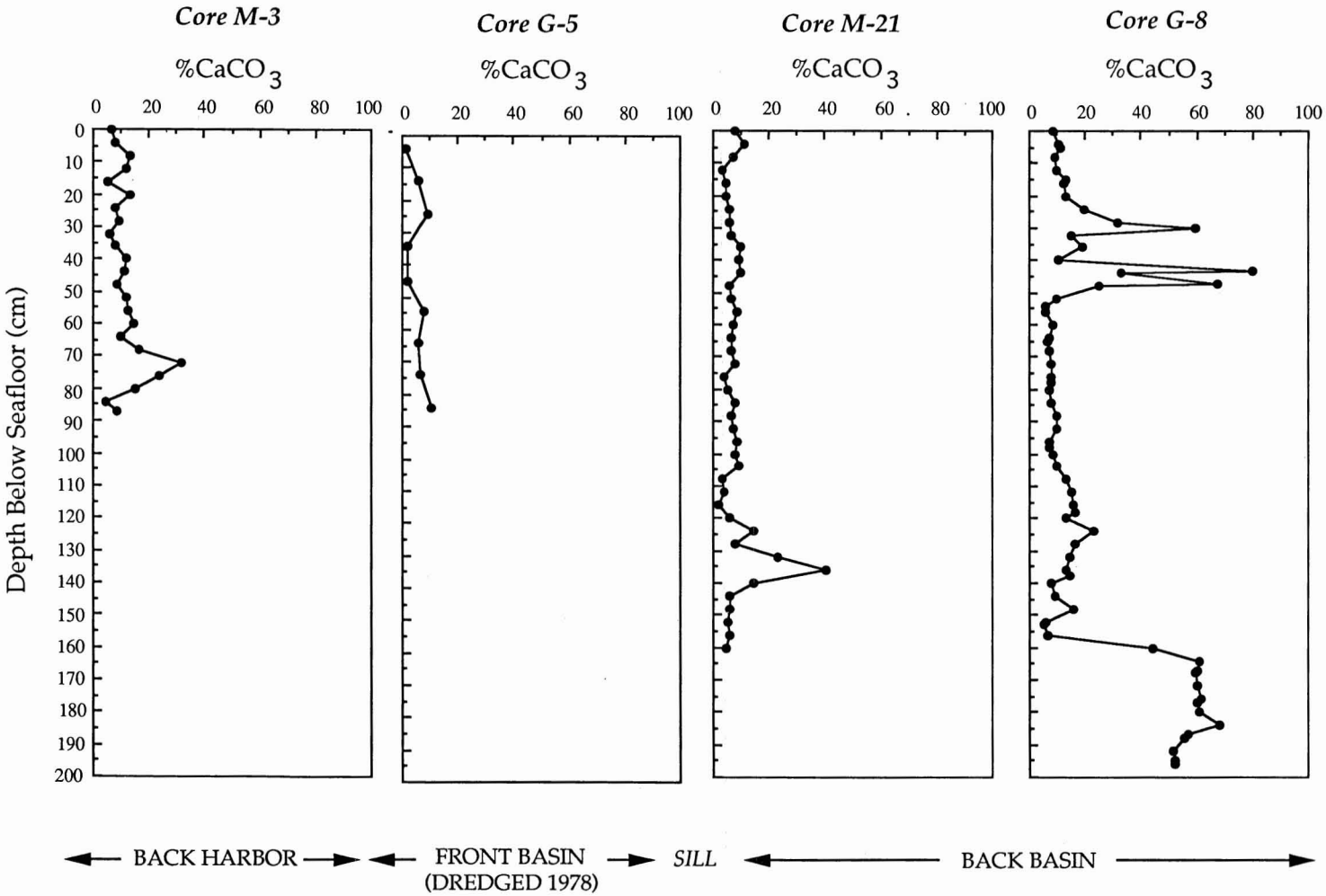

FIGURE 4. Downcore variations in weight percentage $CaCO_3$ for four Ala Wai cores.

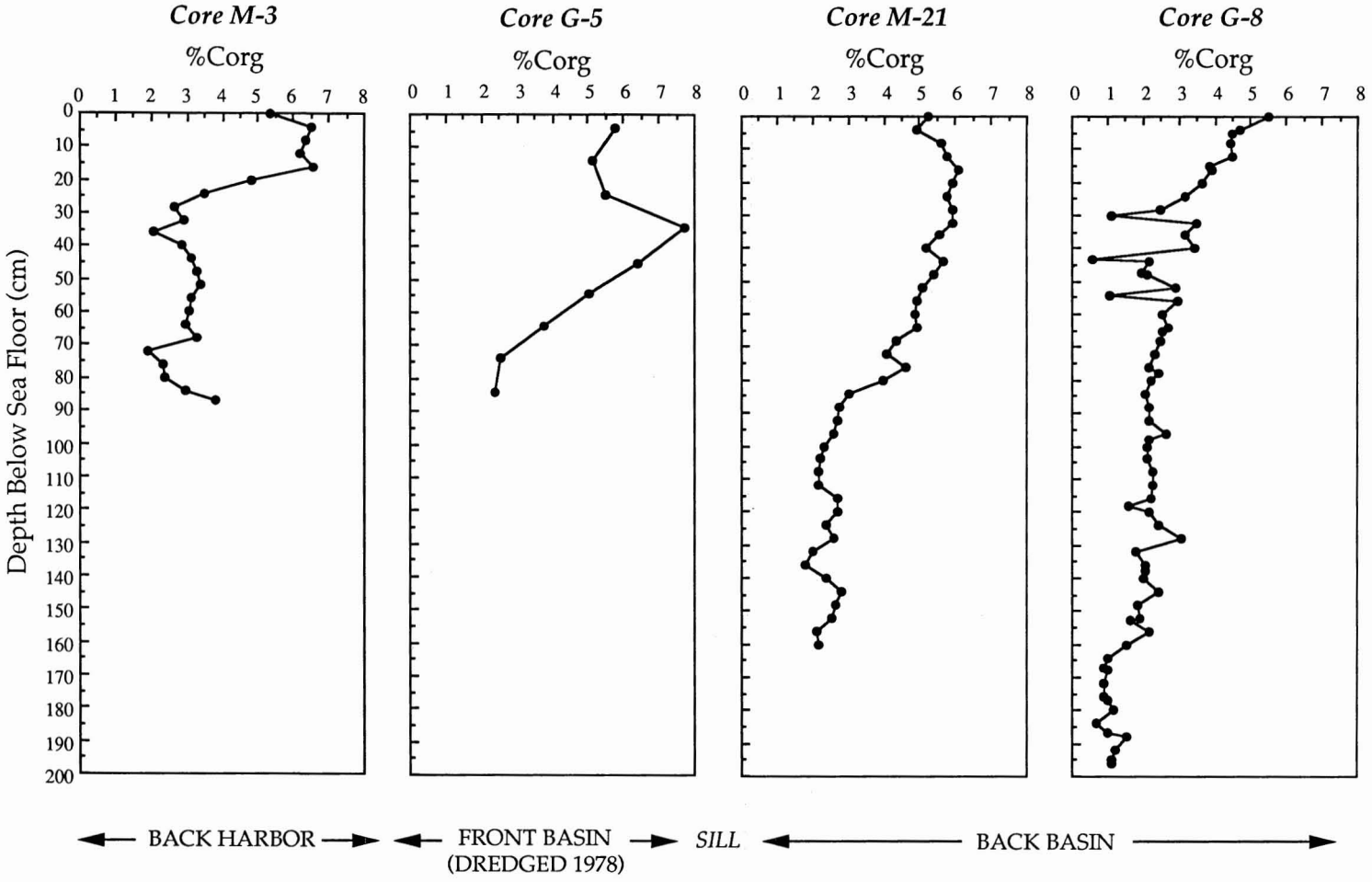

FIGURE 5. Downcore variations in weight percentage organic carbon (Corg) for four Ala Wai cores.

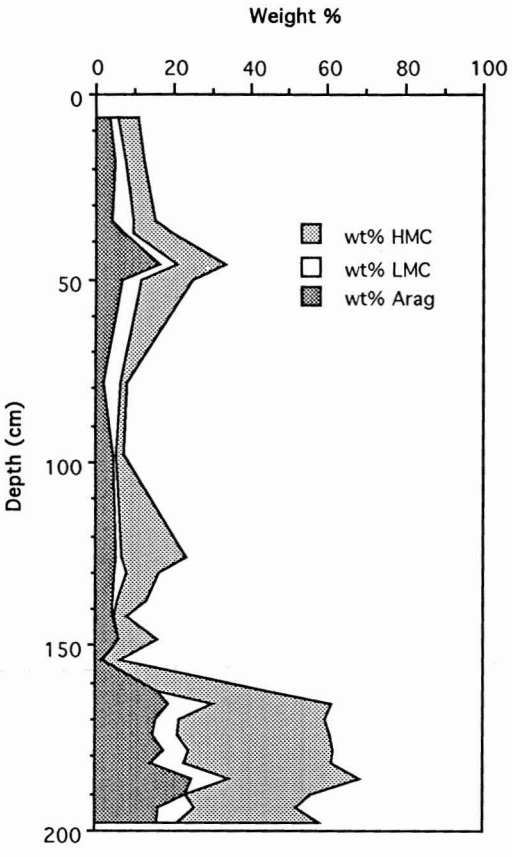

FIGURE 6. Downcore variations in carbonate mineralogy in core G-8. HMC, high-magnesium calcite (magnesian calcite); LMC, low-magnesium carbonate; Arag, aragonite. The width of each field represents the total weight percentage for each mineral.

carbon contents deposited under normal marine conditions (cf. Berner and Raiswell 1984). A cross plot of total organic carbon versus sulfur shows a general linear trend of increase in total sulfur content with increase in organic carbon and an approximately constant C/S ratio close to 1 (Figure 10). Because of the possibility that the uppermost sediments probably have undergone only incomplete diagenesis, the top 15 cm of the core was not used in the carbon-sulfur comparisons. The positive sulfur intercept and C/S weight ratios less than that for Holocene normal marine sediments appear to indicate euxinic (anoxic, sulfidic) bottom water conditions for the basin (cf. Berner and Raiswell 1984, Lyons and Berner 1992); the positive intercept in such cases has been attributed to syngenetic pyrite formation in the water column and at the sediment-water interface, plus early diagenetic precipitation in the pore waters, in a system that shifts from Fe-limitation to C-limitation. However, two observations argue against such a possibility for the Ala Wai back basin. The first is that oxygen depletion does not occur during photoperiods at water depths shallower than 3 m (Laws et al. 1993). The bottom waters, even during peak productivity periods, have around 1 ml liter^{-1} of dissolved oxygen (Gonzalez 1971) and can at best be described as dysaerobic (cf. Stein 1991). The second observation is that model II regression analyses (York 1966, 1969, Sokal and Rohlf 1981; also see Laws and Archie 1981) for the C/S data (Figure 10) indicate that the line of best fit does not have a positive sulfur intercept but is in fact near-zero. It appears, therefore, that the Ala Wai sediments may bear a near-normal marine depositional signature. However, we have not attempted experimentally to determine the proportion of total reduced sulfur in the sediments (cf. Canfield et al. [1986] for technique; Emeis and Morse [1990] and Emeis et al. [1991] for application in organic-rich sediments). Nonetheless, the relatively high concentrations of sulfur and low C/S ratios suggest that, in addition to pyrite, organic sulfur compounds (sulfate esters, C-bonded S) and inorganic adsorbed SO_4^{2-} also likely constitute a rather substantial sulfur pool in these sediments (cf. Losher and Kelts 1989).

Isotopic Composition

Downcore profiles for the isotopic composition of the carbonates, benthic foraminifera, and bulk organic carbon are illustrated in Figure 11. Because the inorganic carbonate fraction in the Ala Wai sediments is an intimate mixture of extremely fine-grained calcite, magnesian calcite, and aragonite, we normalized the isotopic compositions (^{13}C and ^{18}O) with respect to pure calcite, using a mass balance equation:

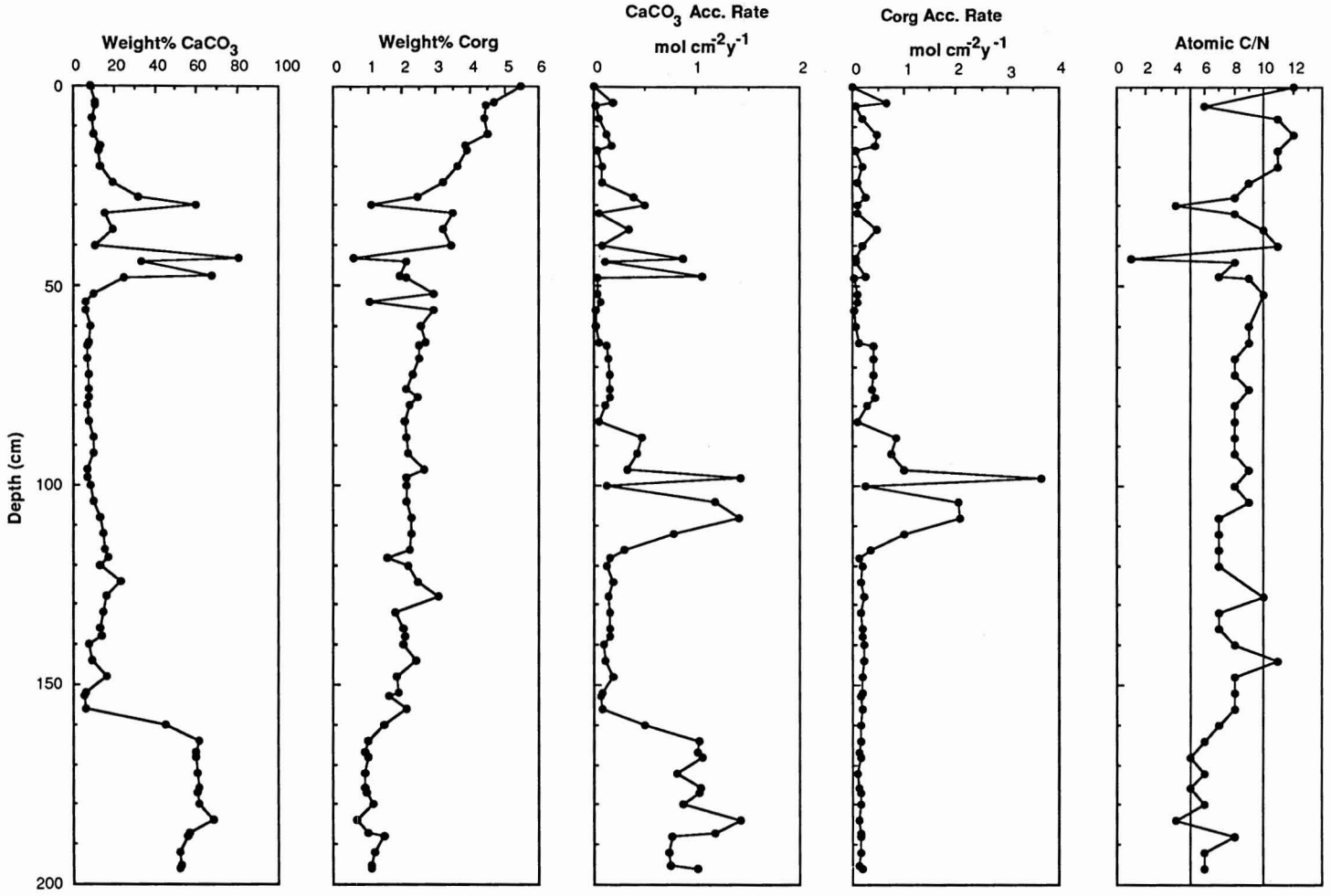

FIGURE 7. Comparison of weight percentage $CaCO_3$, weight percentage organic carbon (C_{org}), atomic organic carbon to total nitrogen ratios, and calculated $CaCO_3$ and C_{org} accumulation (flux) rates for core G-8.

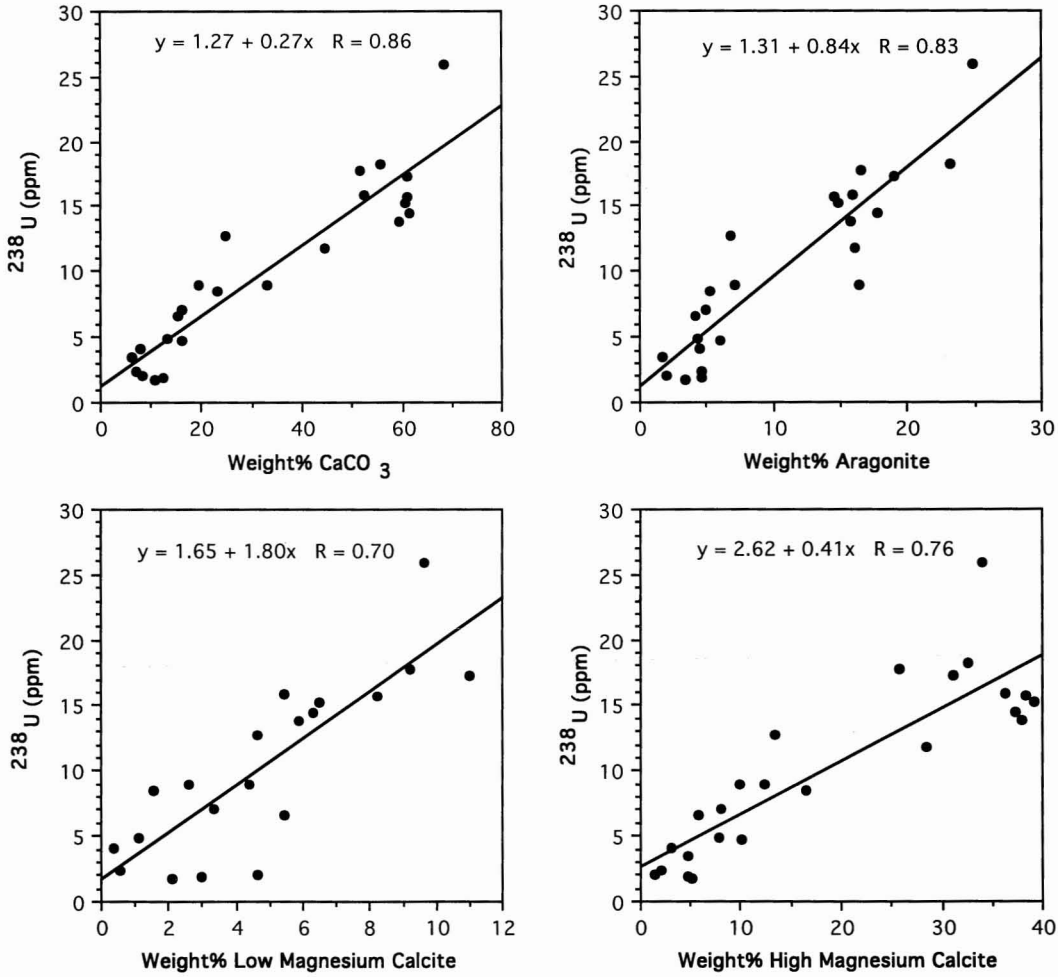

FIGURE 8. Cross plots of ^{238}U concentrations (ppm) versus weight percentage $CaCO_3$, aragonite, low-magnesium calcite, and high-magnesium calcite.

$$n_T\delta_T = n_C\delta_C + n_H\delta_H + n_A\delta_A$$

where n_T, n_C, n_H, and n_A, respectively, refer to the weight % of the bulk carbonate fraction, low-Mg calcite, high Mg-calcite, and aragonite, and δ_T, δ_C, δ_H, and δ_A represent the respective isotopic compositions. The proportions of the various carbonate fractions were determined by X-ray diffractometry, and the following isotopic fractionation factors for a temperature of 25°C (Rubinson and Clayton 1969, Tarutani et al. 1969) were used in the computations: (1) inorganically precipitated magnesian calcite is enriched in ^{18}O relative to pure calcite precipitating under similar conditions by 0.06‰ per mole % $MgCO_3$; and (2) relative to pure calcite, aragonite is enriched in ^{18}O by 0.6‰ and in ^{13}C by 1.8‰.

The carbonates in core G-8 exhibit a depth-dependent grouping of $\delta^{13}C$ and $\delta^{18}O$ values (Figure 11). The upper half of the sediment sequence (0–100 cm) is marked by a downcore decrease in $\delta^{13}C$, with the $\delta^{13}C$ value for the carbonate fraction at a depth of around 100 cm being 2.2‰ more negative

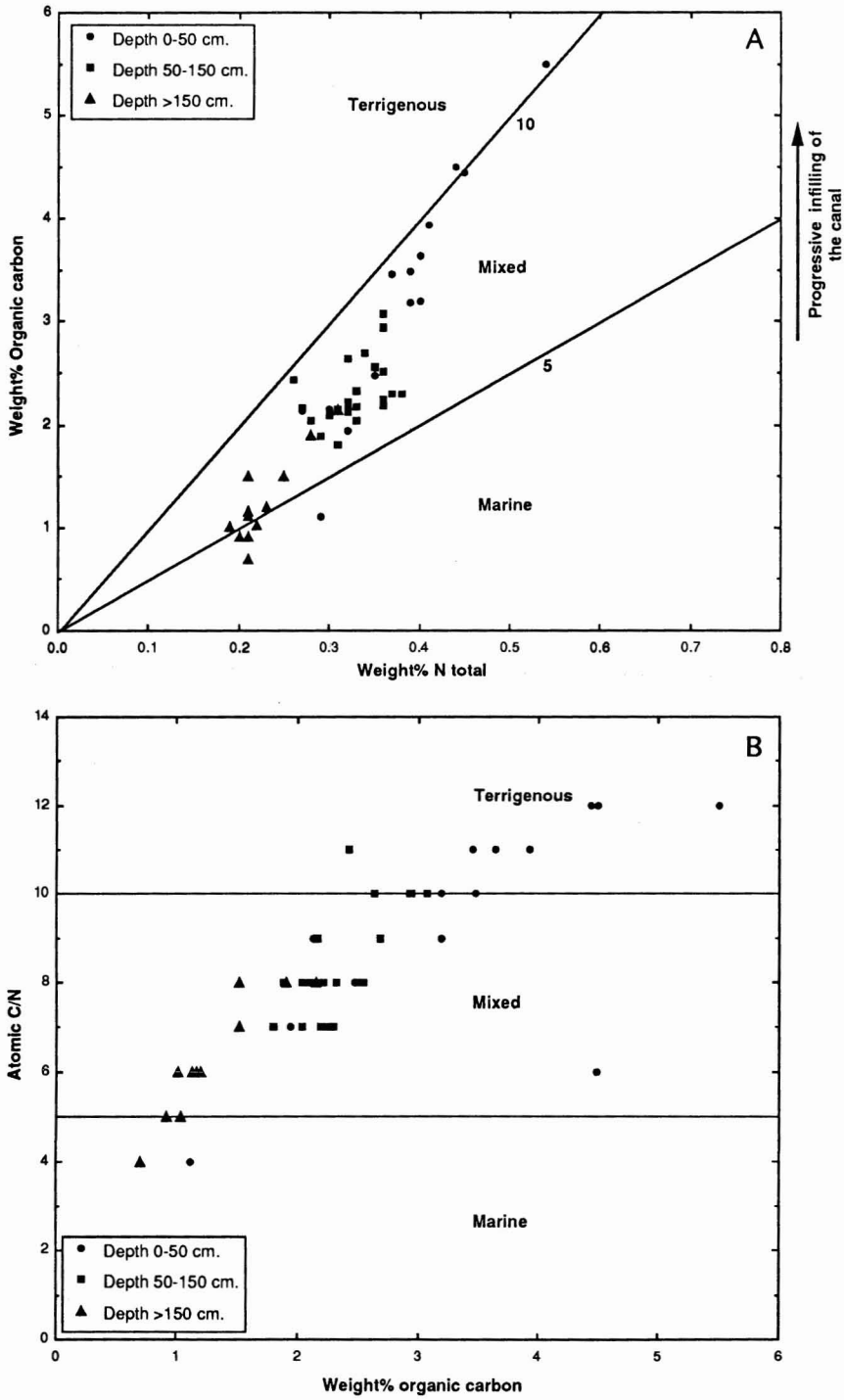

FIGURE 9. (*A*) Weight percentage organic carbon versus nitrogen for core G-8. (*B*) C/N ratios versus percentage organic carbon for core G-8.

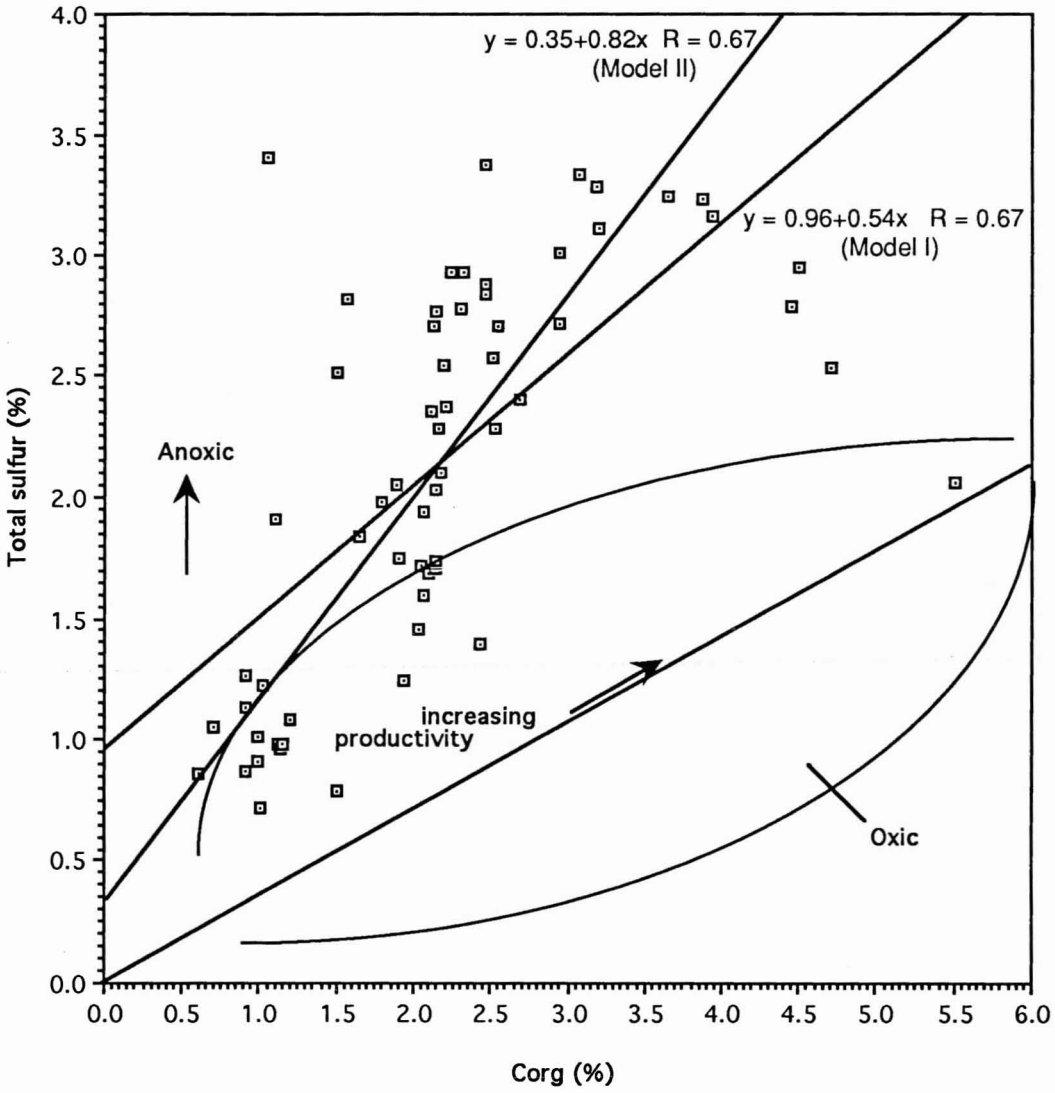

FIGURE 10. Relationship between organic carbon and total sulfur contents in core G-8. Distinction between oxic and anoxic depositional environments according to Leventhal (1983) and Berner and Raiswell (1984). Mean C/S ratio for normal (oxic) marine sediments = 2.8; envelope of regression for normal marine sediments encloses several hundred data points (Berner and Raiswell 1984). Regression line II represents the reduced major axis. Sediments from the top 15 cm of the core were excluded from the calculations.

than in the uppermost sediments. The oxygen isotopic composition of the bulk $CaCO_3$ between 0 and 100 cm shows a corresponding general downcore increase in $\delta^{18}O$. In contrast, below 100 cm, the carbon and oxygen isotopic compositions of the bulk $CaCO_3$ tend to covary positively; $\delta^{13}C$ and $\delta^{18}O$ both increase with depth below 100 cm.

The carbon and oxygen isotopic compositions of the benthic foraminifera are more variable than the corresponding values for the bulk carbonate fraction and are spread

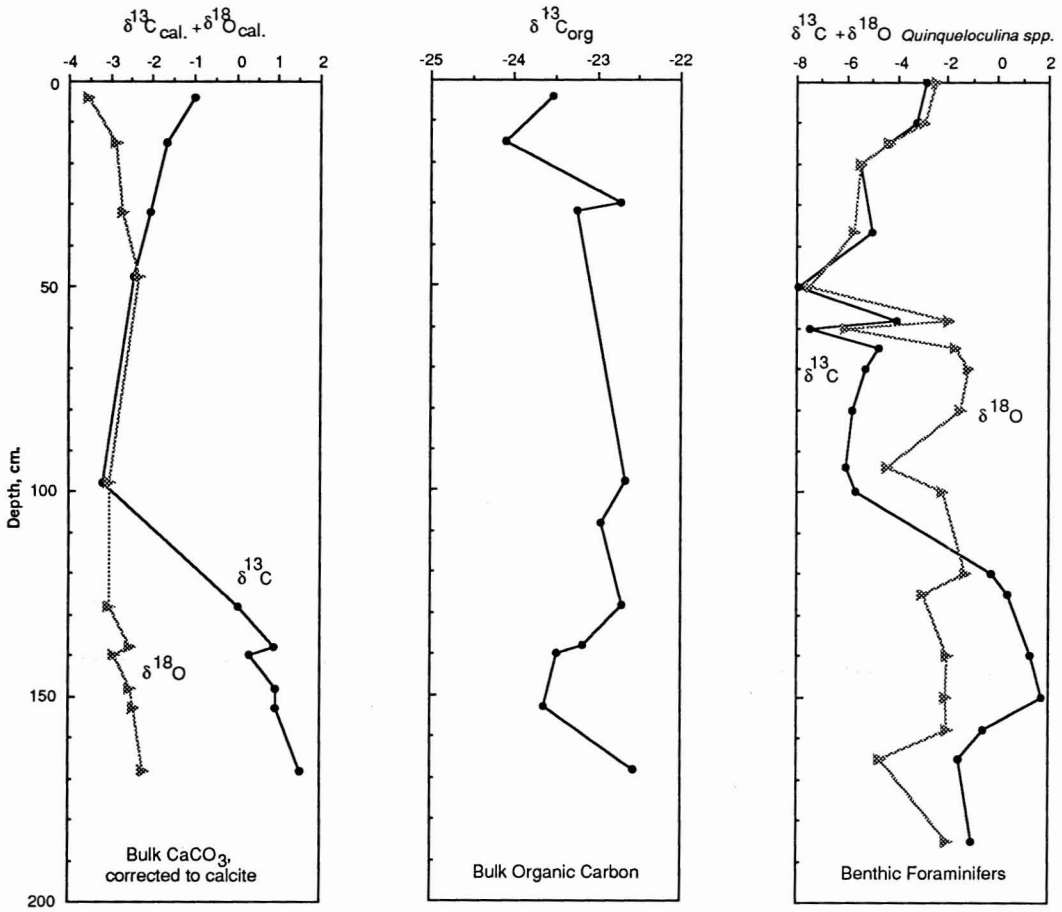

FIGURE 11. Isotopic variations in calcites (*left*), organic carbon (*center*), and in benthic *Quinqueloculina* spp. foraminifers (*right*) in core G-8.

over a wider range (Figure 11). The top of the sediment sequence is marked by an overall downcore decrease in $\delta^{13}C$ and $\delta^{18}O$. Between 100 and 150 cm, values of $\delta^{13}C$ show a progressive increase with depth, whereas values of $\delta^{18}O$ are relatively constant. Below ca. 160 cm, both the isotopic compositions tend to covary again.

The carbon isotopic composition of bulk organic matter is confined to a narrow range of between −22.5‰ and −23.5‰. Between 130 and 150 cm, the values of $\delta^{13}C$ show a progressive decrease with depth, corresponding to the observed downcore increases in $\delta^{13}C$ of the bulk carbonate and of the benthic foraminifers in this section of the core. Although not pronounced, the carbon isotopic composition of the bulk organic matter in the upper 130 cm of the core shows a gradual downcore enrichment in ^{13}C.

DISCUSSION

Several studies have been made of trophic conditions in the Ala Wai Canal based on hydrochemistry and biomass characteristics (cf. Gonzalez 1971, Harris 1975, Cox and Miller 1976, Laws et al. 1993), but no attempt has been made previously to document the variations in its trophic status through time. As explained below, our geochemical analy-

ses of the sediment sequence recovered behind the Ala Wai sill reveal a record of long-term changes in productivity trends on which are superimposed short-term pulses of varying productivity and evaporation rates. In addition, the data indicate two phases of canal eutrophication during the past half century.

Origin of Aragonite, Magnesian Calcite, and Calcite

We hypothesize that the covariance of aragonite and magnesian calcite in the Ala Wai sediments is the result of rapid coprecipitation in response to CO_2 reduction in surface waters as a result of the documented extremely high primary productivity in the canal. The appropriate reactions are as follows:

Photosynthesis:

$$CO_2 + H_2O \rightarrow CH_2O + O_2$$

Carbonate Precipitation:

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O$$

Net Reaction:

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CH_2O + O_2$$

where CH_2O represents sedimentary organic matter. This process is analogous to marine "whitings" and inorganic $CaCO_3$ precipitation in lakes (e.g., Wells and Illing 1964, Friedman 1965, 1993, Kelts and Hsü 1978, McKenzie 1982, 1985, Given and Wilkinson 1985, Shinn et al. 1989, Hollander and McKenzie 1991, Schelske and Hodell 1991, Robbins and Blackwelder 1992, 1993, Hollander et al. 1993, Milliman et al. 1993, Morse and He 1993) and apparently takes place in the Ala Wai despite the high concentration of dissolved phosphate, which tends to inhibit carbonate precipitation (e.g., Walter and Burton 1986). This interpretation of inorganic precipitation is supported by the appreciable lack of biogenic carbonate in the sediments (i.e., trace benthic foraminifer and sponge spicules), the moderately high concentration of carbonate throughout the canal sediments, the fine grain size and mixed marine mineralogy of the carbonates, their marked correlation with large amounts of uranium scavenged from the marine water column, the lack of detectable carbonate in Mānoa-Pālolo Stream sediments, and a positive covariance between $CaCO_3$ and C_{org} accumulation rates in portions of the core G-8 (see below). Furthermore, analysis of the carbon isotopic composition of the total dissolved inorganic carbon (DIC) of water samples collected from the back basin yield a value of −2.49‰. Calcite precipitating in equilibrium with this DIC reservoir should have a carbon isotopic composition of ca. −0.5‰ (Deines et al. 1974, Anderson and Arthur 1983), which roughly corresponds to the isotopic composition of the carbonate in the surficial sediments. In addition to the dominant control exerted by drawdown of P_{CO_2}, increasing temperature and salinity substantially raise the P_{CO_2} at which calcium carbonate nucleation can occur (Morse and He 1993). Thus, supersaturation may also be favored in this basin during periods of net hydrographic deficit, as cations in the surface layer are concentrated and dissolved CO_2 is further removed. As discussed below, it appears that once the precipitation of the carbonates is spontaneously initiated, "crystal breeding" may take place whereby additional precipitation occurs (e.g., Morse and Mackenzie 1990).

Berner's (1978) summary of the laboratory precipitation of magnesian calcites suggests that only under conditions of extreme saturation with respect to calcite ($\Omega > 120$) do inorganic magnesian calcites with greater than 10 mole % $MgCO_3$ precipitate (compare with seawater, which is seven times supersaturated with respect to calcite [Morse and Mackenzie 1990]). In addition, it was also found that these laboratory precipitates only formed under extremely rapid rates of crystallization (in minutes, as with the inorganic whitings reported from the Persian Gulf [Wells and Illing 1964]) and in almost all runs, high magnesian calcite precipitation was accompanied by aragonite, hydrocalcite, or vaterite. Presumably, these rapid crystallization rates also resulted in extremely fine crystallite sizes (e.g., Folk 1974) in the Ala Wai Canal.

Increasing temperature exerts a strong

control on increasing the coprecipitation of magnesium with calcite (see summary in Morse and Mackenzie [1990]). The Ala Wai waters are warm, and the magnesium content of its sediment calcites is high (ca. 14 mole % $MgCO_3$). Harris (1975) and Miller (1975) measured Ala Wai surface water temperatures during 1970–1971 and found them to vary generally between 24 and 32°C (although much lower, anomalous temperatures occasionally were encountered when enhanced inputs of freshwater covered the canal surface). The surface water temperatures and sediment magnesian calcite mole % $MgCO_3$ concentrations of the Ala Wai agree well with recent thermodynamic and experimental data that suggest that magnesian carbonates containing between ca. 9 and 14 mole % $MgCO_3$ precipitate within this temperature range (Burton and Walter 1987, Mucci 1987, Oomori et al. 1987; see Morse and Mackenzie [1990] for summary). Thus, warm surface temperatures appear to have controlled the amount of magnesium substitution in the Ala Wai magnesian carbonates. Aragonite dominates the carbonate suite and likely is the first and most rapidly precipitated carbonate phase (e.g., Walter 1986, Burton and Walter 1987). Aragonite precipitation will raise the Mg^{2+}/Ca^{2+} ratio of the waters, and we suggest that this promotes the subsequent precipitation of magnesian calcite. The origin of the low-magnesium (1–3 mole % $MgCO_3$) calcite is less clear. Some of this may be inorganically precipitated as the precipitation of magnesian calcite progressively lowers the Mg^{2+}/Ca^{2+} ratio of the waters. However, the high concentration of Mg^{2+} in seawater argues against this (e.g., Lippmann 1973, Berner 1975), and we suggest that the bulk of this phase is likely biogenic, as magnesium-bearing Miliolidae foraminifers (cf. Blackmon and Todd 1959; also see Resig et al. 1995) and calcareous sponge spicules (cf. Scholle 1978), both of which occur in the sediments.

U Adsorption

High concentrations of U are typical in reducing sediments, and this is also the case for the Ala Wai Canal (Figure 8). Veeh (1967) studied U deposition in several oceanic anoxic basins and found U concentrations to range from 4.8 to 39 ppm. For sediments deposited in the anoxic environment of Pettaquamscutt River in Rhode Island, Mo et al. (1973) found a direct proportionality between concentrations of organic carbon and uranium, ranging from 7· C_{org} and 7 ppm U to 14% C_{org} and 30 ppm U. For the Ala Wai sediments, however, we found no covariance between weight percentages of U and C_{org}.

The manner in which U is enriched in anoxic to suboxic settings is not clear. Most studies generally suggest that oxidized, soluble U (VI) species ($[UO_2(CO_3)_3]^{4-}$) are removed from seawater through organic complexation, or that U (VI) species flux into pore waters where they are reduced to relatively insoluble U (IV) forms and precipitate as a diagenetic mineral (uraninite? coffinite?) (e.g., Langmuir 1978, Nakashima et al. 1984, Cochran et al. 1986, Anderson 1987, Barnes and Cochran 1990, Thompson et al. 1990), possibly in association with sulfate reduction (Klinkhammer and Palmer 1991, Lovley 1993, Lovley et al. 1993). Inorganic precipitation of UO_2 in association with sulfate reduction may be occurring in the Ala Wai sediments and even perhaps in the water column as a result of the canal's hypereutrophication. Alternatively, U may be sorbed onto rapidly precipitating carbonates in the water column, either through direct adsorption or perhaps as an indirect result of scavenging by organic compounds that are themselves adsorbed to the carbonates. U sorption on particulates is inhibited by its strong complexation with sulfate, fluoride, and carbonate (Langmuir 1978), and it is possible that a combination of sulfate reduction and $CaCO_3$ precipitation act to strongly reduce this sorption barrier in the Ala Wai Canal. The strong covariance between U and $CaCO_3$ (Figure 8) suggests that U adsorption on or into the carbonates may be likely, although, as noted above, we are unsure with which carbonate phase the U is most strongly associated. It is possible that, as with the incorporation of Na^+ and SO_4^{2-} in rapidly precipitated, distorted magnesian

calcites (see Busenberg and Plummer [1989] and references therein), the U is adsorbed into the Ala Wai carbonates along lattice dislocations and plane defects. Alternatively, Morse et al. (1984) have shown through experimental data that, in the presence of $CaCO_3$, uranyl-hydroxy complexes transform to uranyl-carbonate complexes and that these transitions can quantitatively remove U from solution onto a variety of biogenic and synthetic carbonate mineral surfaces; those workers also showed that upon dissolution, Ca^{2+} and uranyl-carbonate were simultaneously released in linear proportions. More work is needed to quantitatively resolve where and how U becomes associated with the carbonates of the Ala Wai Canal.

Assessment of Paleoproductivity

Our hypothesis that the variations in organic carbon and carbonate content in the Ala Wai back basin are the result of historical changes in primary productivity together with variations in the rates of evaporation is substantiated by the record of organic carbon and carbonate accumulation rates in the sediments and the isotopic ratios of the two forms of carbon. The isotopic studies reveal at least two long-term trends in canal eutrophication corresponding to the periods represented by the two halves of the 2-m-deep core G-8. The top 150 cm of the core, composed of sediments deposited in the past 45 yr, bears, in general, imprints of high productivity as revealed by the geochemistry and rates of accumulation of carbonate and organic carbon. The mineralogy and isotopic composition of the carbonates in the lowermost 50 cm of the core, however, point to a phase of high evaporation rates and sustained primary productivity. Superimposed on these long-term trends are several short-period oscillations in the accumulation rates of $CaCO_3$ and C_{org}, which, we demonstrate, were brought about by historical variations in the evaporation-precipitation ratios and freshwater influx into the canal.

CARBONATE AND C_{org} AS INDICATORS OF PRODUCTIVITY. Because authigenic carbonate precipitation and C_{org} preservation in an aquatic environment are intrinsically linked to periods of enhanced productivity, variations in carbonate and C_{org} contents in a sediment sequence may serve as indices of primary productivity. Above, we attributed the carbonate content in the sediment sequence to be primarily a result of changes in physicochemical conditions and abstraction of CO_2 from the system during photosynthesis and evaporation. Similarly, accumulation of major amounts of organic carbon also requires special environmental conditions such as increased surface water production, increased preservation rates of organic matter, and/or rapid burial of organic matter. However, interpretations based solely on organic carbon and carbonate variations are not always straightforward. For instance, cross plots of the carbonate content against organic carbon show a strong negative correlation for 0–25 cm, 25–50 cm, and >150 cm in core G-8 (Figure 12). Such variations may signify (1) dilution effects caused by either changes in carbonate accumulation rate, C_{org} rain rate, or both; (2) changing carbonate flux caused by differences in dissolution rate; or (3) fluctuations in productivity (Arthur and Dean 1991). The absence of dissolution features in benthic foraminifers preserved in the sediments (Resig et al. 1995) discounts dissolution. Strong dilution effects caused by variations in influx of terrigenous organic matter are a distinct possibility, especially because the C/N ratios for the core indicate that the organic matter is not entirely autochthonous. Upsection increases in C_{org} also correlate well with corresponding increases in the terrigenous fraction (increasing C/N ratios) of organic matter, as discussed earlier (Figure 7). Accumulation rates of $CaCO_3$ and C_{org} (Figure 13), on the other hand, display a strong positive correlation for 0–25 cm and between 50–150 cm, indicating that the parallel trend in these portions of the core could be a direct result of enhanced primary productivity (Figure 13*A*, *C*). Because the lack of correlation between $CaCO_3$ and C_{org} concentrations between 50–150 cm tends to discount dilution effects there (Figure 12), the covariance in accumulation rates in this in-

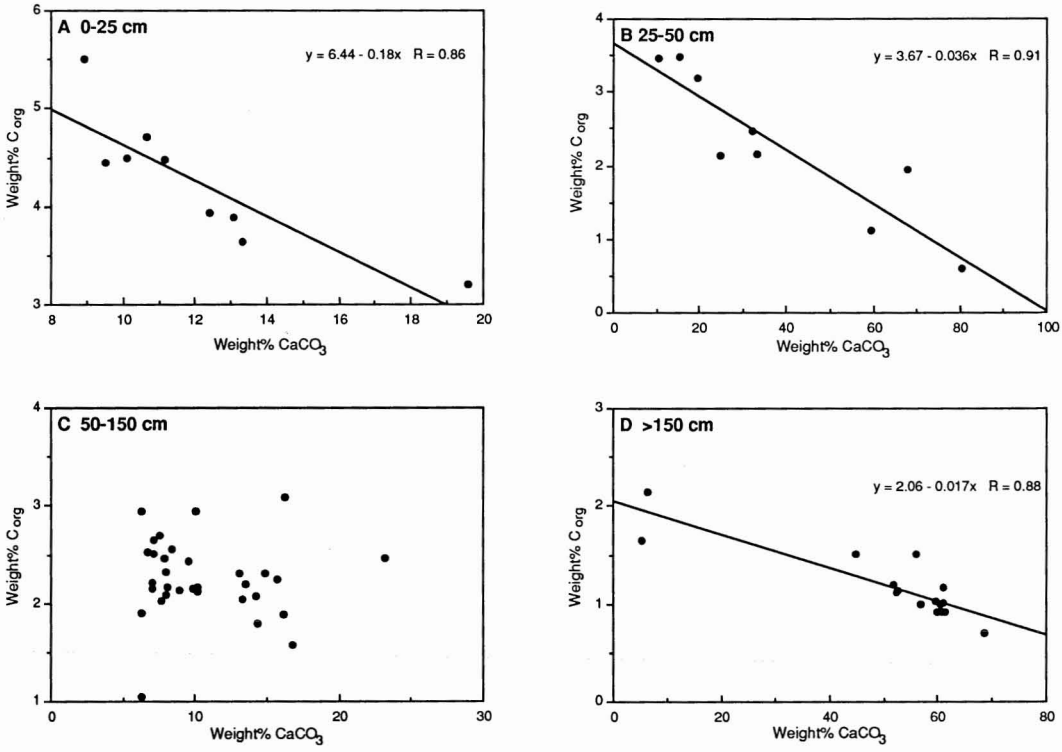

FIGURE 12. Cross plots of weight percentage $CaCO_3$ versus C_{org} for (*A*) 0–25 cm, (*B*) 25–50 cm, (*C*) 50–150 cm, and (*D*) >150 cm in core G-8.

terval can likely be attributed to variations in productivity. The atomic C/N ratios are also nearly constant, indicating lack of variation in terrigenous carbon influx during this period (Figure 9). The covariance in the accumulation rates in the upper 25 cm also suggests recent increases in primary productivity (Figure 13*A*), despite the high C/N ratios in this portion of the core (Figure 7). Further, it is also likely that these uppermost sediments have undergone only incomplete diagenesis and hence preserve appreciable amounts of labile organic carbon as well.

Below a depth of 150 cm, the accumulation rates of $CaCO_3$ and organic carbon are poorly correlated ($r = 0.37$; Figure 13*D*), indicating the possibility that at least a part of the carbonate accumulation may be unrelated to productivity, despite the relatively low C/N ratios (Figure 7), which suggest a predominance of marine organic matter. At least part of this excess carbonate is probably related to aridity and elevated water temperatures during the deposition of this unit (see below). In addition, we further speculate that $CaCO_3$ accumulation rates rapidly outpace organic carbon accumulation rates in this portion of the core because of high rates of spontaneous carbonate precipitation and crystal breeding, whereby first-precipitated crystals in the water column act as templates for additional crystallization and thus reduce the saturation barrier (see Morse and Mackenzie 1990). This process is directly analogous to speeding chemical reactivity and crystal growth in the laboratory through the addition of seed crystals.

Our conversion of core depths to time, as based on cesium-137 ages and assumed sedimentation rates (see above), is illustrated in Figure 14, which contrasts historical trends in rainfall and mean annual temperature in

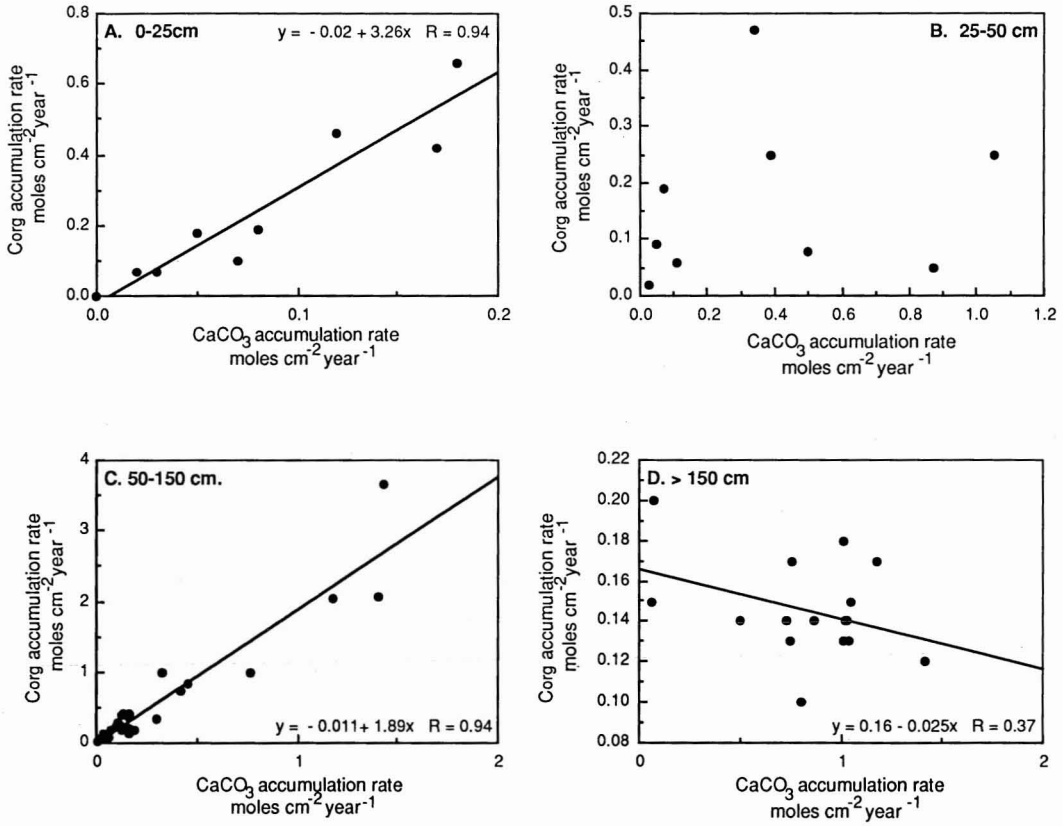

FIGURE 13. Cross plots of accumulation rates of $CaCO_3$ versus C_{org} for (*A*) 0–25 cm, (*B*) 25–50 cm, (*C*) 50–150 cm, and (*D*) >150 cm in core G-8.

Honolulu with the accumulation rates and isotopic results described above. This figure suggests, at first, a rather poor correlation between climate variations and the observed oscillations in carbonate and organic carbon accumulation. The high $CaCO_3$ accumulation rates at the base of the core below 150 cm (corresponding to the years 1935–1947), for example, appear to occur throughout a change from high to low rainfall. State-wide temperature trends (Nullet 1993), however, show general maxima between 1935–1945 and 1970–1985, and these times generally correlate with elevated $CaCO_3$ and C_{org} accumulations in core G-8 (Figure 14). In particular, the period from 1974 to 1991, one of relatively high ambient temperatures and aridity, appears to correspond to the rapid annual fluctuations in the accumulation rates of $CaCO_3$ and C_{org}, observed in the top 50 cm of core G-8 (Figure 14). The high accumulation rates centering between about 1958 and 1964 (between 112 and 64 cm) appear to straddle a period of low rainfall and occur during the onset of a major increase in mean annual temperatures (Figure 14). The relative aridity and the attainment of thermal stratification in the basin during these different time periods are further corroborated by the isotopic composition of the benthic foraminifera as discussed below.

ISOTOPIC COMPOSITION. Bulk analyses of the carbon isotopic composition of primary and diagenetic carbonates can provide valuable information about basin productivity and diagenetic conditions (e.g., Stuiver 1970, Anderson and Arthur 1983, McKenzie 1985,

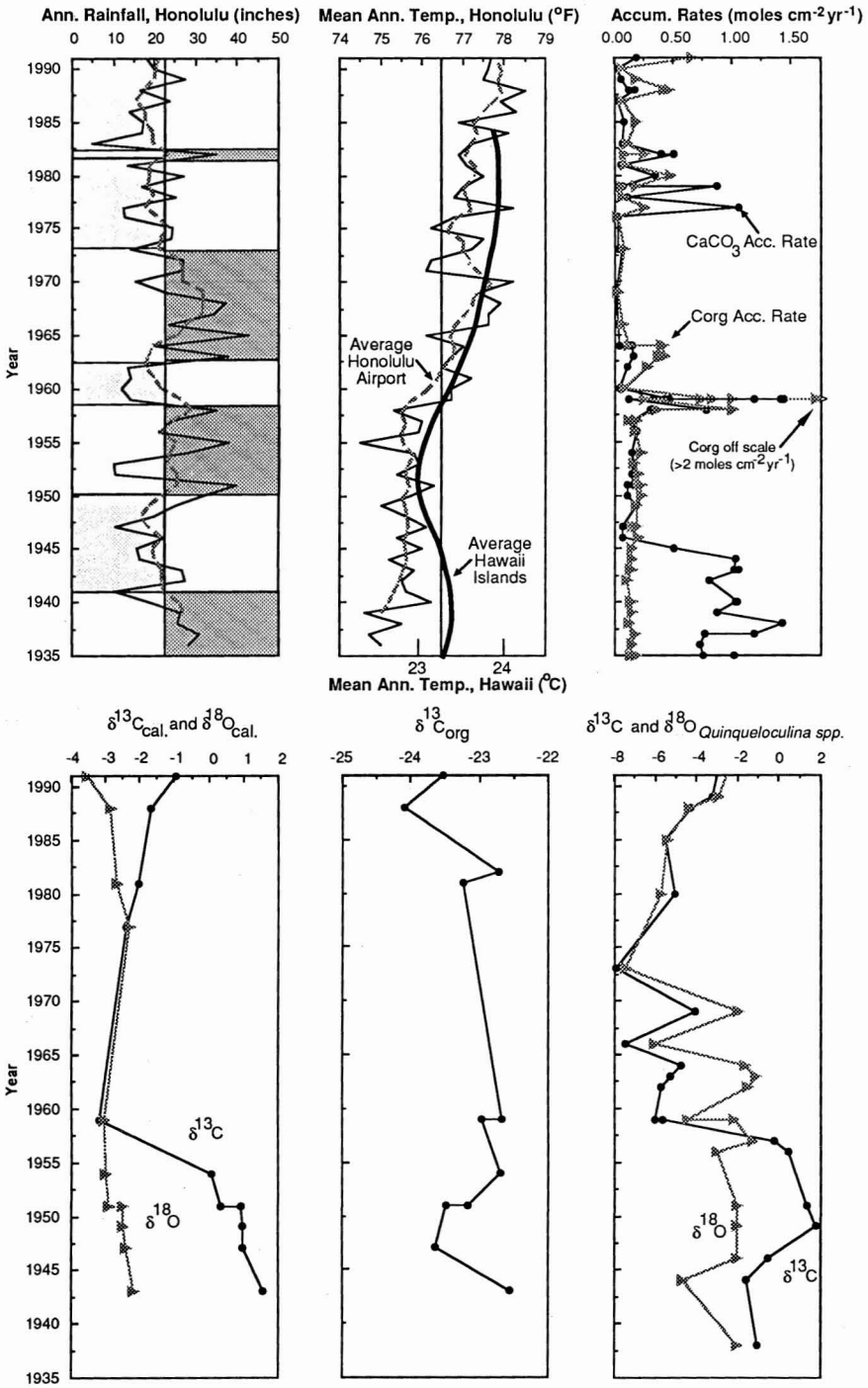

FIGURE 14. Temporal comparison of $CaCO_3$ and C_{org} accumulation rates (*top right*), isotopic variations in calcites (*bottom left*), organic carbon (*bottom center*), and in benthic foraminifers *Quinqueloculina* spp. (*bottom right*) in core G-8, and the historical record of mean annual rainfall (*top left*) and temperature (°F) (*top center*) at the Honolulu airport (State of Hawai'i Data Book 1992: 157–164, Schmitt 1977: 319–324) for the years 1935–1991. Bold line represents a state-wide average of temperature data (°C) corrected for urban heating and changes in station location (Nullet 1993). Dashed lines in the Honolulu airport rainfall and temperature data are calculated 5-yr moving averages; the central vertical lines indicate the 1935–1991 mean for both data sets. Ages based on cesium-137 dating (McMurtry et al. 1995).

Talbot and Kelts 1986, 1990, Hollander 1989, Talbot 1990, Schelske and Hodell 1991, Hollander et al. 1992, 1993). The isotopic composition of carbon in authigenic carbonates precipitated from surface waters is primarily dependent on the isotopic composition of surface water dissolved inorganic carbon (DIC), and, to a lesser extent, on temperature (0.08‰/°C); the former in itself is a complex function of several equilibrium and kinetic fractionation reactions associated with photosynthesis/respiration cycles, exchange rates with atmospheric CO_2, and the composition of the water source (Stiller and Hutchinson 1980). Phytoplankton populations preferentially incorporate isotopically light carbon for photosynthesis, causing the residual DIC in the surface water to become enriched in ^{13}C. Hence, because primary carbonates are a by-product of photosynthetic activity, it follows that as the ^{13}C content of the surface water DIC increases during periods of phytoplankton blooms, the $\delta^{13}C$ of any carbonate that precipitates in isotopic equilibrium with the DIC pool also increases correspondingly. This effect may be heightened in thermally stratified water systems where recycling of the ^{13}C-depleted inorganic carbon from the decomposition of organic matter is inhibited (McKenzie 1985). Thus, an abrupt increase in the $\delta^{13}C$ of the primary carbonate record could be indicative of the attainment of thermal stratification, whereas a gradual increase in $\delta^{13}C$ might mean progressive eutrophication of a stratified basin (Stiller and Hutchinson 1980, Bein 1986). Productivity variations in poorly stratified or nonstratified basins are, however, more difficult to discern from the carbonate isotopic records.

Against the above background, let us now examine the variations in the amount and isotopic composition of the carbonates, benthic foraminifers, and organic carbon. A major change is observed in the $\delta^{13}C$ record of the carbonate fraction at ca. 100 cm (ca. 1959) in core G-8, where it reaches its lowest value of -3.2‰ (Figures 11 and 14). Below that depth, the carbon isotopic values decrease upsection by nearly 5‰, whereas, above that, the values gradually increase toward the top of the core (Figure 11). The gradual increase in $\delta^{13}C$ in the top half of the core indicates a progressive eutrophication of the basin since 1959, as outlined above. Values of $\delta^{13}C$ of benthic foraminifera in the sediment sequence above 100 cm also show an upcore enrichment in ^{13}C since 1959, reflecting the basin's eutrophication through time. Furthermore, these values are markedly more negative than the corresponding $\delta^{13}C$ values of the bulk precipitates, indicating a ^{12}C-enriched bottom-water DIC pool relative to the surficial waters, and therefore the persistence of basin stratification during this period (Figure 11). In contrast to the upcore increases in $\delta^{13}C$ of the carbonates and of the benthic foraminifers, the carbon isotopic composition of the bulk organic matter in the top half of the core shows an overall upsection depletion in ^{13}C, which suggests a gradual increase in the relative contribution of ^{13}C-depleted terrigenous organic matter. As noted previously, C/N ratios for this section of the core also indicate an upcore increase in the terrigenous fraction of the organic matter (Figure 7).

The carbonate mineralogy and accumulation rates of $CaCO_3$ and organic carbon in the sediment sequence below 100 cm reveal two distinct phases in the earlier evolutionary history of the Ala Wai back basin. Although the sediments between 150 and 100 cm bear the normal imprints of sustained biological productivity (i.e., positive correlations between $CaCO_3$ and C_{org} accumulation; Figure 13), below 150 cm $CaCO_3$ and C_{org} accumulation rates do not covary, and there the variations in carbonate mineralogy (high magnesian calcite and aragonite contents; Figure 6) and high $CaCO_3$ accumulation rates (Figure 7) primarily reflect higher water temperatures. The carbon and oxygen isotopic compositions of the carbonates and of the benthic foraminifera (Figure 11) provide further insight into these processes. An upsection decrease in $\delta^{13}C$ of the carbonate fraction between 150 and 100 cm (Figure 11) reflects a progressive decrease in the $\delta^{13}C$ of the water column DIC, brought about by either a decrease in primary productivity between ca. 1947 and 1959, from a greater contribution of oxidized organic carbon to

the DIC pool, or a freshening of the surface waters. The accumulation rates of $CaCO_3$ and organic carbon (Figure 14), however, covary and are nearly constant over a greater part of this interval and show a dramatic increase between 1957 and 1959, signifying a short period of intense productivity at the end of this interval. The carbon isotopic composition of the bulk organic matter also shows upcore enrichment in ^{13}C between 150 and 100 cm, suggesting a progressive increase in primary productivity. In addition, the difference between the $\delta^{13}C$ of the authigenic carbonates and benthic foraminifera ($\Delta\delta^{13}C_{calcite-benthic\ foraminifera}$) gradually increases with time from -0.82‰ in 1949 to 2.47‰ in 1959 (Table 1, Figure 14). This increase in the isotopic gradient between the surface water precipitates and the benthic foraminifera records the gradual development of stratification over this time interval and generally argues against the notion that the $\delta^{13}C$ decrease in bulk carbonates is caused by inputs from oxidized organic carbon. Taken together, these factors indicate a stratified basin and discount a waning of productivity as the cause for the observed upcore $\delta^{13}C$ decrease in bulk carbonates between 150 and 100 cm (Figure 11). As we discuss more fully below, we attribute a progressive decrease in the $\delta^{13}C$ to a progressive freshening of the basin through the 1940s and 1950s.

Cross plots of $\delta^{13}C$ of the carbonate fraction normalized for pure calcite against the corrected oxygen isotopic compositions reveal two distinct and opposing trends for the upper and lower halves of the core G-8, indicating a change in basin hydrology that occurred about 1959 (Figure 15). Before 1959 (below 100 cm depth; Figure 15*A*), a strong positive correlation between $\delta^{13}C$ and $\delta^{18}O$ of the calcite is obvious. Such covariance is characteristic of closed basins and has been attributed to isotopic evolution of waters caused by changes in evaporation and water residence times (Talbot 1990, Talbot and Kelts 1990). In hydrologically open basins with short residence times, the isotopic composition of the water differs little from that of inflow. In contrast, as the residence time of

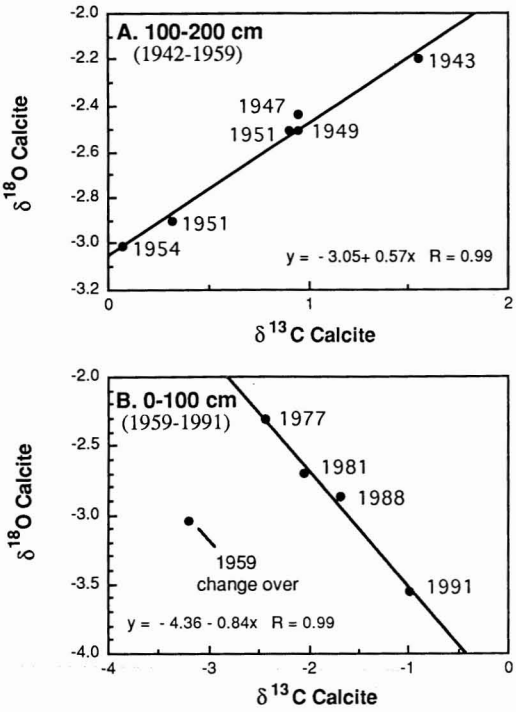

FIGURE 15. Cross plots of $\delta^{13}C$ versus $\delta^{18}O$ for the calcites in (*A*) above 100 cm, and (*B*) below 100 cm in core G-8. The calculated year of deposition for each data point is also shown.

water increases (in closed basins), evaporative concentration may lead to increasing $\delta^{18}O$ values, both for the water and for any carbonates precipitating in equilibrium with it (Fontes and Gonfiantini 1967, Talbot 1990, Leyden et al. 1993). Similarly, in such basins with a negative water balance, evaporative losses also result in a preferential outgassing of $^{12}CO_2$ and consequently a ^{13}C enrichment in the remaining water. Any primary carbonate precipitating in isotopic equilibrium from such evaporative-loss waters will therefore show increasing $\delta^{13}C$ values depending on the intensity of ^{13}C enrichment of the DIC pool.

$\delta^{18}O$ and $\delta^{13}C$ of bulk carbonates are positively correlated below 100 cm in core G-8, with a progressive decrease in both of these isotopes between the years of ca. 1942 and 1959 (Figure 15*A*). This trend is the

opposite of that predicted for closed basins undergoing progressive evaporation described above. Because the development of the Ala Wai sill during this time frame likely caused increased restriction of the back basin, this result at first appears counterintuitive. However, unlike lakes, which may undergo progressive evaporation upon becoming closed basins, the Ala Wai back basin likely became less saline as sill development commenced. Thus, because of this opposite effect of decreasing salinity upon closure, and because local rainwaters have more negative $\delta^{18}O$ and $\delta^{13}C$ values (ca. -4‰ and -7‰, respectively) than does seawater (ca. 0‰ and 0‰, respectively), we attribute the progressive decreases in $\delta^{18}O$ and $\delta^{13}C$ of the Ala Wai carbonates between 1942 and 1959 to a progressive freshening of the back basin over that time period. Two factors seem likely to have caused this freshening: (1) the buildup of the sill, which isolated the back basin from the ocean, and (2) the rapid development of urbanization and consequent runoff from Waikīkī and surrounding catchments.

In contrast to the above, the $\delta^{18}O/\delta^{13}C$ values of bulk carbonate from the upper 100 cm of core G-8 (Figure 15*B*) indicate a less closed basin. The sill was dredged in 1966 and 1978. After the 1978 dredging (Figure 15*B*), the development of open basin conditions in the Ala Wai Canal is reflected in a negative correlation between the carbon and oxygen isotopic compositions of the carbonate fraction (Figures 11 and 15*B*). It is also interesting that our geochemical studies point to a progressive development of eutrophic conditions in the canal beginning after 1978. We contend, therefore, that after the last dredging of the canal, a major phase of gradually increasing productivity began the early part of the last decade and has been continuing ever since.

CONCLUSIONS

Variations in geochemistry and carbonate mineralogy of the sediments cored from the hypereutrophic Ala Wai Canal point to a record of historical changes in biological productivity and evaporation-precipitation ratios during the past ca. 64 yr of the canal's existence. In addition to the high percentages of detrital components in the canal, relatively high concentrations of organic carbon (ca. 1–8%), calcium carbonate (ca. 6–68%), and abundant diatom tests and pyrite characterize the sediment assemblage in this estuary. The carbonate fraction is an intimate mixture of aragonite (ca. 2–25%), magnesian calcite (ca. 1–38%), and calcite (0–11%). The covariance of carbonate in the sediments appears to be a direct result of rapid coprecipitation of aragonite and magnesian calcite in response to CO_2 abstraction from the aquatic system during periods of intense photosynthesis and evaporation. The accumulation of authigenic carbonates may also be heightened by further and more rapid carbonate precipitation (crystal breeding) on the freshly precipitated crystals. A mixed marine/terrigenous type of organic matter with a general dominance of the terrigenous fraction is characteristic of the entire sediment sequence in the back basin. Although the sediments display a near-normal marine depositional signature, a higher enrichment in sulfur relative to comparable lithologies from the marine realm points to a possible abundance of organic sulfur and inorganic adsorbed sulfate phases in the sediments. The record of organic carbon and carbonate accumulations in the sediments, the carbon and oxygen isotopic compositions of the carbonate fraction and of the benthic foraminifera, and variations in carbonate mineralogy reveal three long-term trends in the trophic status and water-mass stratification of the back basin, corresponding to the periods between ca. 1935–1947 (sediments below 150 cm), 1947–1959 (150–100 cm), and after 1959 (<100 cm). Superimposed on these long-term trends are several short-term pulses of inter-annual variations in basin productivity, which might be related to brief climatic fluctuations.

Below 150 cm, the anomalously high magnesian calcite and aragonite contents in the sediments, the relatively high accumulation rates of $CaCO_3$, and a weak negative correla-

tion between $CaCO_3$ and C_{org} accumulation rates point to a phase of relative aridity and elevated water temperatures during the deposition of this unit. This conclusion is further substantiated by the maximum enrichments in the heavy isotopes of carbon and oxygen of the bulk carbonate fraction in this interval, compared with the other sections of the core. A predominance of autochthonous organic matter in these sediments also invokes sustained levels of biological productivity during that earlier period.

The period between 1947 and 1959 (core G-8, 150–100 cm) represents an interval of sustained biological productivity as reflected in the uniform rates of accumulation of $CaCO_3$ and C_{org} and their positive covariance. An increase in the isotopic gradient between the surface water carbonate precipitates and the benthic foraminifera recorded between 150 and 100 cm documents the development of water-mass stratification during the 1950s. The strong positive covariance in the $\delta^{13}C$ and $\delta^{18}O$ of the carbonates in the entire lower half of core G-8 (100–200 cm) reflects a progressive freshening of the back basin between 1943 and ca. 1959. The development of this basin hydrography is related to the rapid development and growth of the sedimentary sill at the mouth of the Mānoa-Pālolo Stream drainage canal and increased urbanization with consequent increases in freshwater runoff into the canal.

The third long-term trend in the evolutionary history of the Ala Wai back basin is represented by a phase of increasing productivity and eutrophication of the basin since ca. 1959, as reflected in the geochemistry of the sediments above 100 cm. The relatively high contents of $CaCO_3$ and C_{org} and the overall good positive correlation between the accumulation rates of these two forms of carbon testify to a period of elevated levels of productivity. The gradual upsection increase in values of $\delta^{13}C$ of the carbonate and benthic foraminifer fractions indicates the progressive eutrophication and water column stratification in the back basin of the canal over the past 20 yr. The progressive decrease in the $\delta^{18}O$ of bulk carbonates over this same interval again records the renewed buildup of the canal's sediment sill and the consequent freshening of the back basin behind it.

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